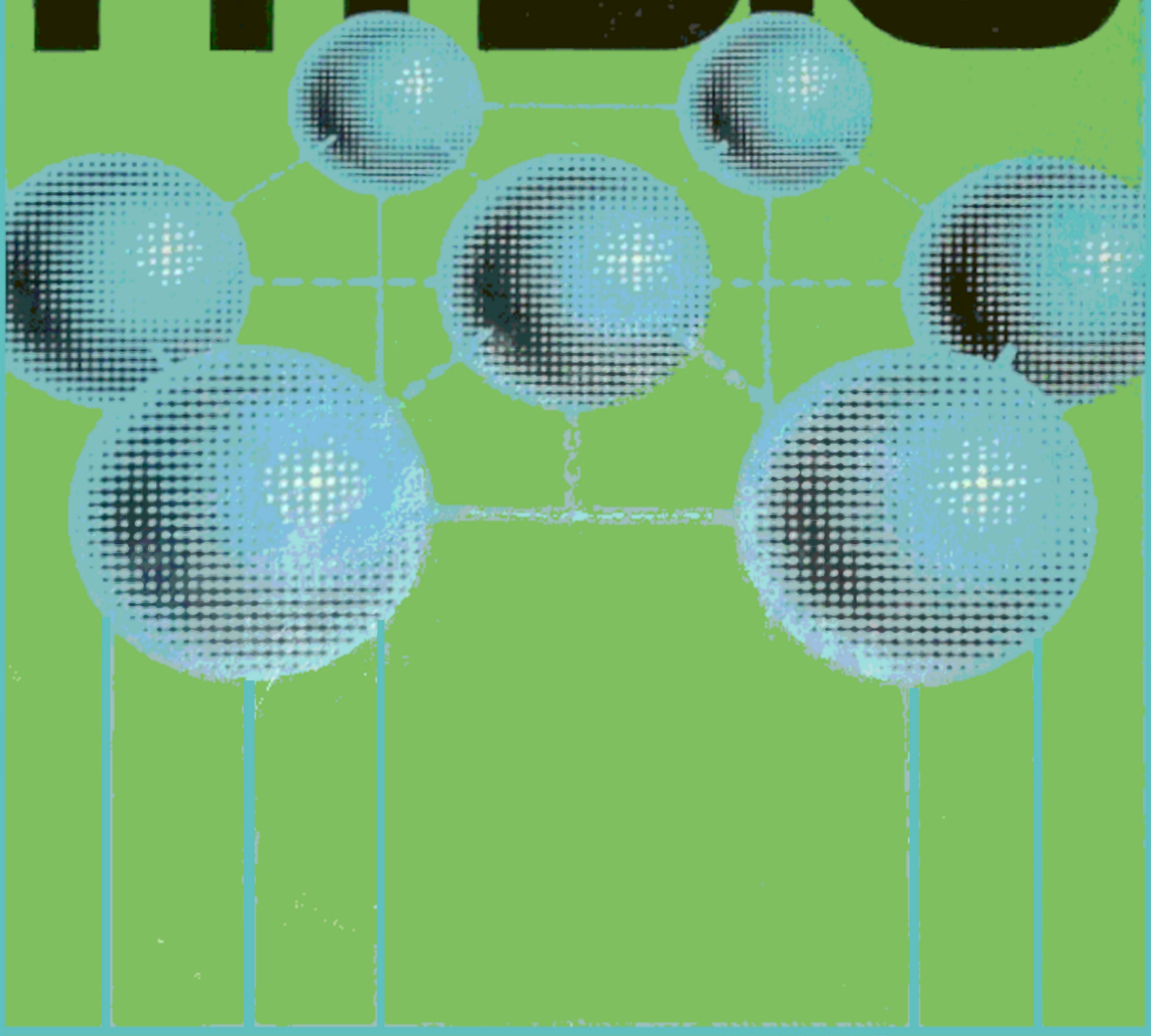
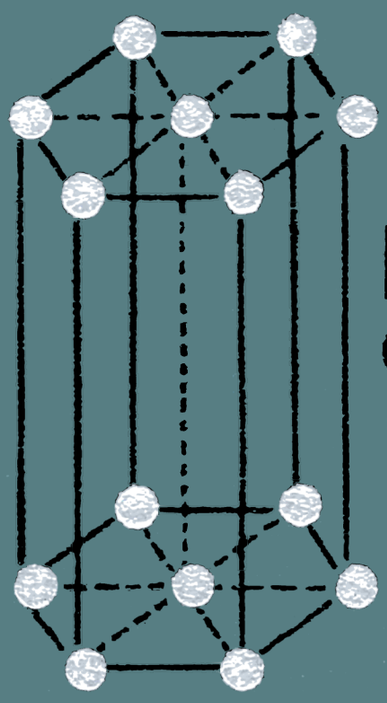
Yu. I. Sirotin, M. P. Shaskolskaya

FUNDAMENTALS OF CRYSTAL PHYSICS



Mir Publishers Moscow

Sirotin
Shaskolskaya



FUNDAMENTALS OF CRYSTAL PHYSICS

Yu.I. Sirotin
M.P. Shaskolskaya

FUNDAMENTALS OF CRYSTAL PHYSICS

Translated
from the Russian
by
Valentina Snigirevskaya

Mir
Publishers
Moscow

First published 1982
Revised from the 1979 Russian edition

На английском языке

© Главная редакция физико-математической литературы
издательства «Наука», 1979

© English translation, Mir Publishers, 1982

ИЗДАТЕЛЬСТВО МИР

Ю. И. Сиротин
М. П. Шаскольская

ОСНОВЫ КРИСТАЛЛОФИЗИКИ

Издательство «Наука»
Москва

CONTENTS

Preface to the Second Russian Edition 9
Excerpts from the Preface to the First Russian Edition 10
List of Notation 13

Chapter *I.* **Basic Information on Crystallography** 17

1. Crystal Structure and Space Lattice 17
2. Crystallographic Projections 23
3. Simple Finite Elements of the Symmetry of Crystals 27
4. Crystallographic Categories and Systems 42
5. Point Groups of Crystal Symmetry (Symmetry Classes) 47
6. Derivation and Description of 32 Classes of Crystal Symmetry (32 Point Groups of Symmetry) 55
7. Limit Groups of Symmetry (Curie Groups) 68
8. Symmetry of Crystal Structure 71
9. Combinations of the Symmetry Elements of Structures. Bravais Lattices. Generation of New Symmetry Elements 74
10. 230 Space Groups of Symmetry 84
11. Mutual Vector Basis and Reciprocal Lattice 88
12. Indexing of Directions and Planes in Crystals 92
13. Transformation of Indices with a Change of the System of Coordinates 101
14. Symmetrically Equivalent Sets of Planes and Directions. Simple Crystal Forms 114
15. Some Problems of Geometric Crystallography 125

Chapter *II.* **Coordinate Systems, Vectors and Tensors** 134

16. Cartesian Coordinate Systems 134
17. Orthogonal Transformations 137
18. Second-Rank Tensors 144
19. Eigenvectors and Eigenvalues of a Symmetric Second-Rank Tensors 147
20. Small Changes of a Symmetric Second-Rank Tensor 152
21. Normal and Tangential Components of a Second-Rank Symmetric Tensor 155

22. External Symmetry and Representation of Vectors and Second-Rank Symmetric Tensors 159
23. Axial Vectors 165

Chapter III. **Introduction to Crystal Physics. Electrical and Thermal Properties of Crystals** 174

24. Anisotropic Continuous Media 174
25. The Symmetry Principle in Crystal Physics 182
26. Fundamental Equations of Electrostatics of Crystals 188
27. Symmetry of the Dielectric Properties of Crystals 191
28. Crystals in a Uniform Electric Field 196
29. The Field in a Spherical Gap in an Anisotropic Medium 201
30. Fields of a Point Charge and a Dipole in an Anisotropic Medium 204
31. Pyroelectrics 207
32. Direct Electric Current in Crystals 210
33. Thermal Conductivity of Crystals 212

Chapter IV. **Optical Properties of Crystals** 216

34. Electromagnetic Waves in Transparent Crystals . . . 216
35. Optical Indicatrix 220
36. Waves and Rays. Principle of Duality. Fresnel's Ellipsoid 227
37. Solution of the Problem of Light Propagation in a Crystal in an Arbitrary System of Coordinates 232
38. Fresnel's Equation. Wave and Ray Surfaces 236
39. Interconnection Between the Optical Surfaces in Crystals. Conical Refraction 240
40. Observation of the Optical Anisotropy of Crystals in Polarized Light 245

Chapter V. **Symmetry of Higher-Rank Tensors** 253

41. Tensors and Pseudotensors of Higher Ranks 253
42. Internal Symmetry of Tensors and Duality Relations . . 257
43. Non-Coordinate Notation of Tensors. Invariant Differential Operations on Tensors 263
44. External Symmetry and Representation of Tensors and Pseudotensors 266
45. Method of Direct Verification 275
46. Cyclic Coordinates. Hermann's Theorem 281
47. Application of the Theory of Group Representation to the Problems of Tensor Symmetry 287
48. The Isotropic and Gyrotropic Tensors 301

Chapter VI. **Elasticity of Crystals** 308

49. Small Strains of a Continuous Medium 308
50. Stress Tensor 314
51. Generalized Hooke's Law 319
52. Symmetry of the Elastic Properties of Crystals . . . 324
53. Simple States of Stress 330
54. Bending and Twisting of Crystals 339
55. Temperature Stresses in Crystals 350
56. Elastic Waves in Crystals 358

Chapter VII. **Thermodynamics of Crystals** 380

57. Internal Energy and Thermodynamic Potential of a Crystal 380
58. Piezoelectric Effect and Its Symmetry 386
59. Simultaneous Solution of the Equations of the Electro- and Elastostatics of Crystals 396
60. Invariant and Non-Invariant Thermodynamic Potentials and Their Matrices 406
61. Dependence of Thermodynamic Coefficients on Conditions of Measurement 411
62. Elastic Waves in Piezoelectric Crystals 416
63. Thermodynamic Inequalities 419
64. Alterations of Crystal Symmetry in Phase Transitions of the Second Kind 423
65. Changes of the Physical Properties of Crystals Under Phase Transitions of the Second Kind 430
66. Mathematical Methods of the Theory of Phase Transitions 445

Chapter VIII. **Magnetic Symmetry in Crystal Physics** 456

67. Time Reversal and Antisymmetry 456
68. Point Groups of Magnetic Symmetry 460
69. Space Groups of Magnetic Symmetry—Shubnikov's Groups 466
70. Magnetic Symmetry of Crystals 470
71. Geometric Realization of the Expanded Orthogonal Group 476
72. Tensors Defined on an Expanded Orthogonal Group . . 479
73. Piezomagnetic and Magnetoelectric Effects 485

Chapter IX. **Effects of the Higher Orders** 488

74. Thermodynamic Consideration of Non-Linear Effects . . 488
75. Piezoresistive Effect 491
76. Onsager Reciprocal Relations and Thermogalvanomagnetic Effects 493
77. Electrooptical and Piezooptical Effects 503
78. Artificial Optical Anisotropy of Crystals 508

79. Non-Linear Polarization in Case of Propagation of Electromagnetic Intense Waves 515
80. Generation of Light Harmonics. Directions of Synchronism 519
81. Optical Activity of Crystals 525
82. Artificial Optical Activity 540
83. Acoustic Activity of Crystals 545

Chapter *X.* **Some General Problems of Crystal Physics** 551

84. Extreme-Value Problems of Crystal Physics 551
85. The Problem of Comparing Tensor Properties of Crystals 555
86. The Problem of Choosing Standard Crystallographic and Crystal-Physical Systems of Coordinates . . . 561
87. Functional Relations in Crystal Physics 566

Appendices 581

A. Crystallographic and Crystal-Physical Systems of Coordinates . 581
B. Bravais Lattices and Crystallographic Matrices 581
C. Properties of Directions in Crystals 590
D. Analytical Proof of Theorems on the Multiplication of Symmetry Operations 597
E. Tensors Invariant with Respect to Crystallographic and Limit Groups
F. Contracted Notation of Tensors 627

References 637
Index 646

PREFACE TO THE SECOND RUSSIAN EDITION

The principal author of this book, Yuri Isakovich Sirotin (1923-1974), had untimely passed away before the first edition came off the press. Many of his creative ideas remained unrealized. The final preparations of the manuscript for the first edition and the revision of the work for the second edition had to be done without him. The responsibility for all the possible faults and failures of the book is all mine.

Numerous minor corrections, changes and some abridgements have been made for the second edition, but on the whole the construction of chapters and sections, the numeration of equations and tables remain unchanged. The need to curtail the size of the book called for the elimination of the tables of numerical experimental data defining various physical properties of crystals.

A subject index has been added. Some additions to the list of references have not made it exhaustive; it contains only the principal monographs and papers mentioned in the book.

The manuscript has been reviewed by the Department of Crystal Physics of the Moscow State University (Head of Department—prof. I. A. Yakovlev) and the Department of Crystallography of the Leningrad State University (Head of Department—prof. V. A. Frank-Kamenetsky) and has been recommended as a textbook for physics specializations at the higher educational institutions.

I am grateful to the reviewers and all persons who have sent their comments on the first edition, especially to T. N. Tarkhova.

M. P. Shaskolskaya

EXCERPTS FROM THE PREFACE TO THE FIRST RUSSIAN EDITION

Within the last 15-20 years experimental crystal physics has emerged from the academic boundaries of a few research laboratories into the wide world of practice. The new, rapidly developing branches of science and technology, such as quantum electronics, quantum and non-linear optics, production of semiconductor instruments, piezotechnology, acoustics, etc., all involve the use of monocrystals and their singular peculiarities, as well as the use of new crystal-physical phenomena which are being discovered in rapid succession. Books on crystal physics have become an imperative necessity. The success of Nye's textbook (1967), whose two Russian editions soon went through, was not accidental. However, there appears to be necessary, along with Nye's book, a fuller and more detailed work, even though it may be less suitable for those becoming initially acquainted with the subject.

It was the authors' intention that the present monograph should satisfy this need. In preparing the book, the authors wished to combine the general physical with the symmetric approach, this being the distinctive feature of the Soviet school of crystal physics, founded by A. V. Shubnikov. The authors tried their best to utilize and promote A. V. Shubnikov's ideas throughout the whole book.

This book has developed from the lectures and practical courses on crystallography and crystal physics delivered by the authors at the Moscow Institute of Steel and Alloys and at the Department of Crystal Physics of the Moscow State University.

Structural crystallography and crystal chemistry, structure-sensitive properties, defects and the growth of crystals were deliberately omitted from the book. Moreover, the size of the book and the manner of presentation prevented the inclusion of experimental measurement methods and of the examples of the practical application of the described physical properties of crystals. The recent publication of a book on problems in crystal physics (by Perelomova and Tagieva, 1972), edited by one of the present authors, partly compensates for the lack of problems in our book which were left out for reasons of space.

Only those essentials of geometric crystallography have been included here which are necessary in crystal physics; the well-known

comments of academician N. V. Belov (1957, 1958) on the crystallography course for physicists have been taken into account.

Only those topics of the extensive material on tensor calculus have been chosen which are important for crystal physics, some of them are barely mentioned in the existing books. Along with the coordinate (index) representation of tensor relations, non-coordinate representation is also used in our book, thus allowing the reader to decide which of the representations is more convenient in each particular case. Notation used by different authors for non-coordinate representation is of two types: the first one is used, for instance, in monographs by F. I. Fedorov (1958, 1965), the second one, derived from Gibbs, is applied in the course by Borisenko and Tarapov (1966) and in monographs by Lurie (1955, 1970). The notation of the second type is used in this book, since it is suitable for tensors not only of the second but also of the higher ranks. The theory of group representations is not described in our book, because it is used in those rare cases when it would be difficult to do without it.

In the course on crystal physics the influence of the symmetry and dissymmetry of crystals on their basic physical properties is emphasized, especially the anisotropy of these properties. In this respect there turns out to be a similarity of properties that are essentially different in other respects, such as diffusion and dielectric permittivity, magnetostriction and piezooptical effect. A description of the anisotropy of one of these properties can be applied to a considerable extent to another property, at least qualitatively. The quantitative characteristics of anisotropy greatly change, however, from property to property and from substance to substance. Such data can be found in handbooks, e.g. Landolt-Boernstein (1966, 1969, 1971), Krishnan (1958), Voronkov, Grechushnikov, Distler, Petrov (1965) and in reviews, which served as a basis for the compilation of illustrative tables of material constants of crystals, permitting the reader to obtain an idea of the magnitude of an effect and its anisotropy.

For giving a lucid idea of the anisotropy of physical properties of crystals our book contains illustrations that characterize it: representation surfaces, their sections and stereographic projections. Some of them have been taken from literature, while others were calculated and drawn, under the guidance of one of the present authors, by Sh. M. Butabayev and L. G. Yanusova in cooperation with P. L. Rubin*. The authors are deeply grateful to them for their great and difficult work which has contributed considerably to the improvement of our book.

---

* Sh. M. Butabayev drew Figs. 24.2, 24.11, 47.5*a*, 54.3, 54.10, 58.2, 58.3, 81.2; L. G. Yanusova, Figs. 44.1, 47.2, 47.3, 47.4, 47.5*b*, 47.6, 54.4, 54.5, 54.6, 54.7, 54.8, 56.3.

Elastic properties were chosen as the principal object for demonstrating the anisotropy of the physical properties of crystals, since they are comparatively simple and well known. Strain tensor and not the displacement vector was chosen as the basic characteristic of strain, this allowing brevity of description and demonstration of the similarity between the basic equations of electro- and elastostatics. A comprehensive description of various phase transitions with a double change of symmetry (Ch. VII, Sec. 65) is a methodological novelty; it shows that within the boundaries of the applicability of the theory, all changes of the properties of crystals in phase transition depend on the groups of the symmetry of the phases connected by the given transition.

The appendices mainly contain reference data related simultaneously to several sections of our book.

The authors together drew up the plan and discussed the contents of all sections of the book, and in many cases it is difficult to determine the extent of the contribution of each of them. Chapters I. III and IV were written mainly by M. P. Shaskolskaya, and the rest largely by Yu. I. Sirotin.

The authors are grateful to S. A. Akhmanov, L. K. Zarembo, V. A. Koptsik, V. K. Semenchenko, M. M. Umansky, with whom they discussed individual sections of the book, as well as to V. A. Frank-Kamenetsky, V. A. Bokov, and V. N. Rozhansky who took the trouble of reviewing the book. The authors thank their former students E. Bartenev, N. Voropayeva, S. Orlov, G. Titova and V. Shcherbakov.

Yu. I. Sirotin, M. P. Shaskolskaya

LIST OF NOTATION

For the notation of the symmetry elements see Sections 3 and 8, Tables 3.1 and 8.1, for those of the symmetry classes (point groups) see Secs. 5, 6, 8, Tables 6.1, 6.2, 6.3, 8.1; for notation of the antisymmetry elements see Sec. 67; for those of space groups see Sec. 10; for those of the point groups of magnetic symmetry see Sec. 69; for those of Shubnikov's group see Sec. 69.

For Miller and Bravais symbols see Secs. 12 and 13, Table 13.1. Miller and Bravais symbols for planes and faces are given in parentheses (...), symbols of directions or edges are given in brackets [...], of a simple form or a set of symmetrically equivalent directions are given in braces {...}, of a bundle of symmetrically equivalent directions are in French quotes ⟨...⟩. The minus sign in a symbol is over a digit.

Vector notation is in semi-bold type italics of the Latin alphabet, for instance $\boldsymbol{p}$, $\boldsymbol{n}$, $\boldsymbol{V}$.

Tensor notation is in semi-bold type ordinary letters of the Latin alphabet and semi-bold type letters of the Greek alphabet, for instance s, **T**, $\boldsymbol{\varkappa}$.

Scalar (dot) product is denoted by a dot ($\cdot$), vector product by an oblique cross ($\times$).

Two dots (:) denote a double-dot product of tensors, three dots ($\vdots$) are a component product of tensors.

Two identical vector notations together (e.g., **kk**, **mm**) signify a tensor product of a vector multiplied by itself (see Sec. 18). [V], [V^2], etc. are Jahn symbols (see Sec. 42). Operators within a group are listed in braces.

$\subset$—symbol of the inclusion of a subgroup into a group

$\in$—symbol of belonging to a group, of inclusion into a set

$\cap$—symbol of the group intersection

$\subseteq$—symbol of a non-strict inclusion into a group

$\boldsymbol{I}$—unit tensor

δ^{α}_{β}, δ_{ij}—Kronecker's tensor

$\delta^{\alpha\beta\gamma}$, $\delta_{\alpha\beta\gamma}$, δ_{ijk}—Levi-Civita pseudo-tensor

$\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$—base vectors of a lattice

$\boldsymbol{a}^1$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3$—base vectors of a reciprocal lattice

$\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$—mutually orthogonal unit vectors of the Cartesian coordinate (usually crystal-physical) system

X, Y, Z—crystallographic axes

X_1, X_2, X_3—axes of the Cartesian coordinate (usually crystal-physical) system

$P^{\beta}_{\alpha'}$, $Q^{\alpha'}_{\beta}$, $P^{\mu}_{\lambda'}$, $Q^{\lambda'}_{\mu}$—transformation matrices of common rectilinear coordinates

$c_{i'j}$—matrix of the transformation of Cartesian coordinates (matrix of cosines)

$r_{i'j}$—matrix of rotation of Cartesian coordinates

$\boldsymbol{E}$—electric-field vector

$\boldsymbol{H}$—magnetic-field vector

$\boldsymbol{D}$—electric-field induction vector

$\boldsymbol{P}$—polarization vector

$\boldsymbol{\varkappa}$, $\varkappa_{ij}$—tensor of dielectric permittivity

$\boldsymbol{\eta}$, η_{ij}—tensor of dielectric impermeability

$\boldsymbol{\lambda}$, λ_{ij}—tensor of thermal conductivity coefficients

$\mathbf{k}$, k_{ij}—tensor of thermal diffusivity coefficients

$\boldsymbol{\rho}$, ρ_{ij}—tensor of specific resistance

$\boldsymbol{m}$—wave normal unit vector

$\boldsymbol{s}$—ray unit vector

N_o, N_e—principal refractive indices of uniaxial crystals

N_1, N_2, N_3 or N_g, N_m, N_p—principal refractive indices of biaxial crystals

n_1, n_2 and n_o, n_e—refractive indices for an arbitrary direction of light propagation

χ—character of representation (Secs. 47 and 66)

$\boldsymbol{u}$—displacement vector

$\boldsymbol{\varepsilon}$, ε_{ij}, ε_{λ}—small strain tensor

$\boldsymbol{\omega}$, ω_{ij}—small rotation tensor

$\mathring{\boldsymbol{\varphi}}$, $\mathring{\varphi}_i$—small rotation axial vector

$\boldsymbol{\sigma}$, σ_{ij}, σ_{λ}—stress tensor (in Secs. 32 and 76—electric conductivity tensor)

α, α_{ij}—thermal expansion tensor (in Secs. 26, 27 and 80—tensor of dielectric susceptibility, in Sec. 76—tensor of thermoelectric coefficients)

$\mathbf{s}$, s_{ijkl}, $s_{\lambda\mu}$—tensor of elastic compliance coefficients

$\mathbf{c}$, c_{ijkl}, $c_{\lambda\mu}$—tensor of elasticity coefficients

U—internal energy per unit volume

Φ—thermodynamic potential per unit volume

S—entropy per unit volume

T—temperature

C—heat capacity per unit volume

$\mathbf{d}$, d_{ijkl}, $d_{i\mu}$—tensor of piezoelectric coefficients

x_A, x_a—generalized thermodynamic coordinates

X_A, X_a—generalized thermodynamic forces

$\mathbf{\Pi}$, Π_{ijkl}, $\Pi_{\lambda\mu}$—tensor of piezoresistive coefficients

$\mathbf{m}$, m_{ijkl}, $m_{\lambda\mu}$—tensor of elastoresistive coefficients

J_a—generalized fluxes in thermodynamics of irreversible processes

K_a—forces conjugate to fluxes in the thermodynamics of irreversible processes

L_{ab}—kinetic coefficients

$\boldsymbol{\pi}$, π_{ijkl}, $\pi_{\lambda\mu}$—tensor of piezooptical coefficients

$\mathbf{p}$, p_{ijkl}, $p_{\lambda\mu}$—tensor of elastooptical coefficients

$\mathbf{r}$, r_{ijkl}, $r_{\lambda\mu}$—tensor of electrooptical coefficients

$\mathbf{K}$, K_{ijkl}, $K_{\lambda\mu}$—tensor of Kerr coefficients

χ, χ_{ijk}—tensor of quadratic dielectric susceptibility

θ, θ_{ijkl}—tensor of cubic dielectric susceptibility

$\mathbf{G}$, G_{ij}—pseudotensor of gyration

Indices:

α, β, $\gamma = 1, 2, 3$ correspond to the axes of the crystallographic system of coordinates, they can be written as superscripts or as subscripts

i, j, k, $l = 1, 2, 3$ correspond to the Cartesian (usually crystal-physical) system of coordinates

λ, μ, ν, $\varkappa = 1, \ldots, 6$ allow the replacement of two tensor indices by one; in the main part of the text (beginning with Ch. VI) they are written as subscripts, while in the Appendix both as superscripts and subscripts

A, B, C, $D = 0, 1, \ldots, 9$—in the notation of generalized thermodynamic forces and coordinates, including temperature and entropy, and in the corresponding thermodynamic matrices (Ch. VII)

$a, b, c, d = 1, 2, \ldots, 9$—in the notation of generalized thermodynamic forces and coordinates, excluding temperature and entropy, and in the corresponding thermodynamic matrices (Ch. VII and Sec. 74)

$a, b, c, d = 1, 2, \ldots, 9$—in the notation of generalized fluxes, forces conjugate to them, and matrices of kinetic coefficients (Sec. 76)

Cases when the indices are used in a different sense or have other meanings are specified in the text.

Chapter I

BASIC INFORMATION ON CRYSTALLOGRAPHY

Sec. 1. Crystal Structure and Space Lattice

"Crystal physics investigates the regularities of physical phenomena in crystals connected with the internal symmetry of crystals and their discrete atomic structure" (Shubnikov, 1956).

"Symmetry is the basic feature of crystals" (Shubnikov, 1960).

The spatial relations of atoms and interatomic forces characterize the orderliness, regularity and symmetry of the internal structure of crystals. Particles that compose crystals, i.e. ions, atoms, molecules, aggregates are regularly and symmetrically arrayed in space in the form of orderly rows, nets, lattices. Due to the regularity and symmetry of the internal structure both the physical properties of crystals and the polyhedral external forms of crystals are also symmetrical.

The regularity and symmetry of crystal structure are the result of the dynamic equilibrium of many forces and processes. External influences, such as electric and magnetic fields, some mechanical force or an alien atom in a crystal can somewhat disturb this dynamic equilibrium and correspondingly change the properties of the crystal. This opens up wide opportunities for controlling the properties of crystals used in technology.

The homogeneity, discreteness and anisotropy of crystals result from the regularity and symmetry of their structure.

Generally speaking, points in a crystal are different: in one point there can be located a particle of one kind (let us say, the Na nucleus in the structure of NaCl), while in another a particle of another kind (the Cl nucleus), in a third one there are no nuclei at all, but it is characterized by a definite quantity of an electric potential, while the fourth by another its quantity, and so on (Fig. 1.1).

On the whole, however, a crystal is homogeneous—any of its parts is neither worse nor better than all the other parts*. Homogeneity of a crystal is manifested by the existence of a so-called *radius of homogeneity*, R: no matter where the sphere of radus R is located in a crystal, it will contain along with any point a similarly located

* Here and elsewhere we do not discuss any defects of crystal structure, i.e. an ideal crystal is meant. In any real crystal there are disturbances of structure resulting from the conditions of its growth and previous history, i.e. mechanical, thermal and other treatment of the crystal.

one (or, as it is conventionally called, a point *homologous* to it), i.e. in a sphere of homogeneity there are at least two Na nuclei, two Cl nuclei, etc. The radius of homogeneity is usually several angstroms long, as has been shown by X-ray analyses. At the same time the crystal is discrete—any point of it can be surrounded with a sphere of discreteness of such a small radius that there will be no homologous point within it. The radii of discreteness vary for different points of a crystal, but they are always smaller than the radius of homogeneity (Fig. 1.2).

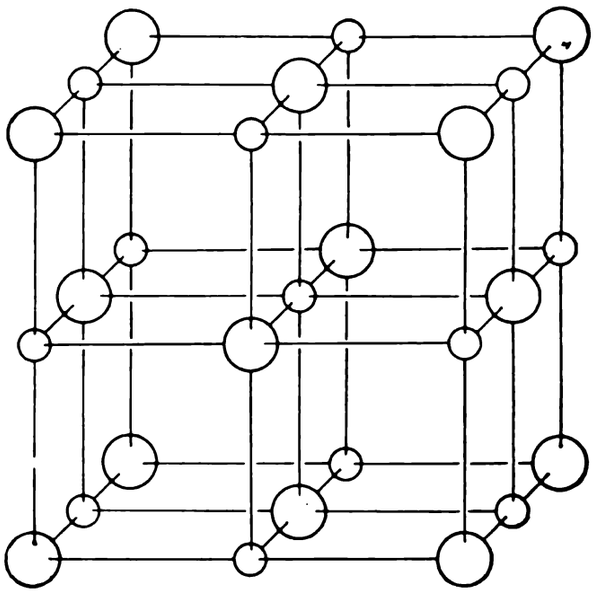


Fig. 1.1. Structure of rock salt (sodium chloride)

Let us, from the very beginning, emphasize the dual approach to the description of a crystal substance: crystals can be regarded both as discrete (i. e. discontinuous) and continuous media. The discreteness of internal structure naturally means that the properties

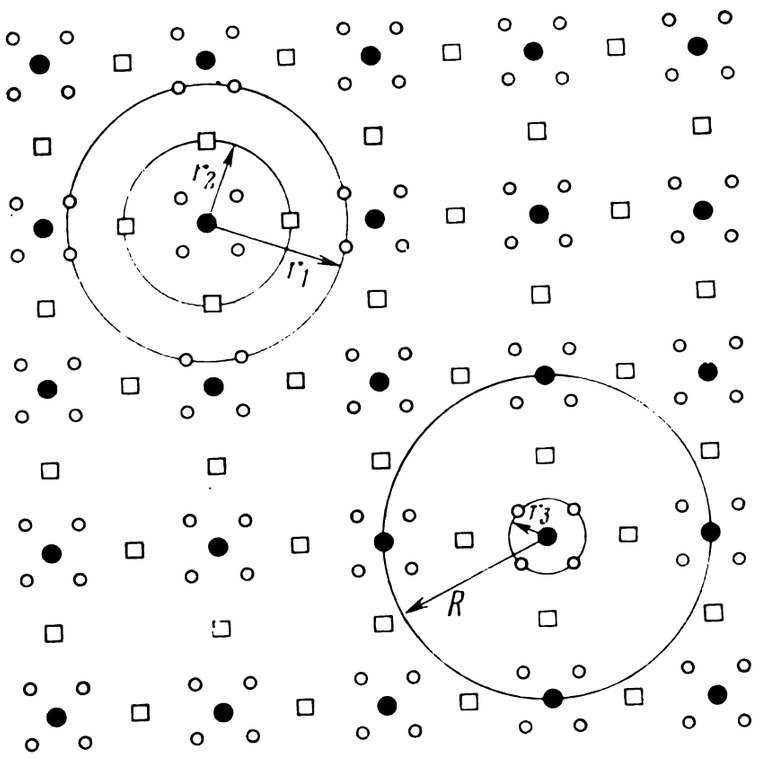


Fig. 1.2. Radius of homogeneity R of crystal space and radii of discretion r_1, r_2, r_3 of its individual points

of crystals cannot be similar at the places with particles and at those without them, or at places with particles of different kinds. However, it will suffice for the description of many properties of cryslals to

discuss volumes considerably larger than the volume of a particle proper and considerably smaller than that of a crystal as a whole. It is just this conception that allows us to regard a crystal as a continuous and homogeneous medium.

Anisotropy is the dissimilarity of properties in different directions. Almost all the properties of a crystal vary in different directions (but are the same in symmetric directions) because in crystal structure the distances and bonds between particles vary in different directions. The growth rate of a crystal is also anisotropic: it is just for this very reason that a crystal grows in the shape of a regular polyhedron.

When a crystal grows, particles of matter from its environment are deposited on its faces, and the faces grow parallel to themselves. The areas of faces as well as their shape can change, individual faces can be supplanted by the adjacent ones and be overgrown, but the mutual inclination of faces remains unchanged. Therefore any crystal substance can be unambiguously specified by the mutual inclination of its faces.

Angles between respective faces of crystals are constant in all crystals of a given substance under similar conditions*. This is the *law of the constancy of angles in crystals* discovered by Nicholas Stenon in 1669 on the basis of his observations of natural polyhedral crystals.

This law is due to the correspondence of the faces of a crystal polyhedron to the plane atomic nets in the crystal structure. Angles between the planes are a characteristic feature of the structure of a given crystal substance, depending on the bonds between particles constituting a crystal. These angles are at present measured and determined with the aid of X-ray photographs irrespective of whether or not a crystal has a regular external form.

The faces of crystal polyhedrons correspond to the planes consisting of material particles, the edges of a crystal, to the rows of material particles. The mass centres of particles constitute rows, plane nets, crystal lattices.

In the structure of an ideal crystal all homologous (similarly arrayed) points are arranged in infinite, regularly repeating symmetric rows (Fig. 1.3). The points of crystal space are anisotropic, therefore they are better to be pictured as asymmetrical shapes, although in most cases, for greater simplicity, we shall depict them as dots or small circles. The shortest distance between homologous points in an indefinitely extended row is called the *shortest*, or *basic*, *translation*, *a*, or the *period of translation*, the *period of the identity of a row*, the *parameter of a row*. In crystal structure this is the inter-

* If a substance has several polymorphous modifications, one definite modification is meant each time.

atomic distance. Rows, nets and crystal lattices are considered to be infinite.

Symmetric transformation, repeating a point (or a small sphere) in space without rotation, i.e. a parallel transfer is called *transformation by translation*, or simply *translation**. Repeating any point

Fig. 1.3. Symmetric infinite row

by translation we obtain an infinite periodic row of homologous points at distances $-na, \ldots, -a, 0, a, 2a, 3a, \ldots, na, \ldots$. Translation $\boldsymbol{a}$ is the characteristic of this row. Homologous points interconnected by symmetric transformation by translation $\boldsymbol{a}_1$ are called *points* of a row. The point of a row, as well as the point of a plane net or space lattice, does not necessarily coincide with a material particle.

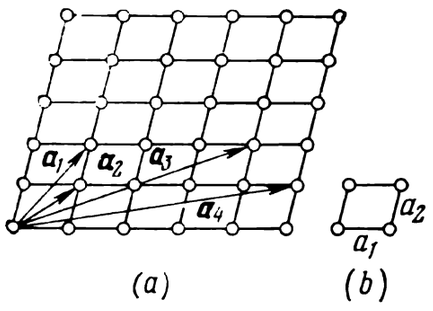


Fig. 1.4. Symmetric infinite plane net: (a) different choice of elementary translations $\boldsymbol{a}_1, \boldsymbol{a}_2, \ldots, \boldsymbol{a}_5$; (b) primitive cell constructed on the smallest translations and corresponding to the net symmetry

By repeating the points of a symmetric row with the aid of another translation, $\boldsymbol{a}_2$, not parallel to the first one we obtain a system of homologous points in the form of a *plane net* (Fig. 1.4). A two-dimensional plane net is completely defined by two translations, $\boldsymbol{a}_1$, and $\boldsymbol{a}_2$ or by three arbitrary points not lying on a straight line. Parallelograms whose vertices are points are called *cells* of a plane net. Any pair of translations not lying on one straight line will repeat the homologous points in the form of a plane net, but it has been convened to choose, as the basic parameters of a plane net, the so-called *elementary translations* as the shortest ones and reflecting the symmetry of the net. A pair of elementary translations, $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$, completely defines the pattern of the repetitions of homologous points in a plane.

A cell whose sides are elementary translations is called a *unit cell* of a plane net. A unit cell is *primitive* if it has no points inside. The area of a primitive cell is equal to the area per point of the net, i.e. it is a constant quantity.

* The term 'translation' has two meanings: (1) symmetric transformation representing a finite parallel displacement, (2) the shortest distance in a row of homologous points.

Infinite repetition of a point by three non-coplanar translations will produce a *space lattice*, i.e. a three-dimensional symmetrical system of homologous points. The three basic translations, $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, of a space lattice can be chosen in many ways, but just as for a plane net, it has been convened to choose the shortest translations that represent the lattice symmetry in the best possible manner.

A parallelepiped whose sides are three elementary translations is called a *unit cell* or an *elementary parallelepiped.* An elementary parallelepiped is primitive if it has no points inside.

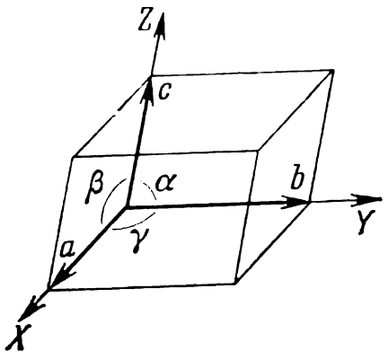


Fig. 1.5. Elementary parallelepiped (standard notation)

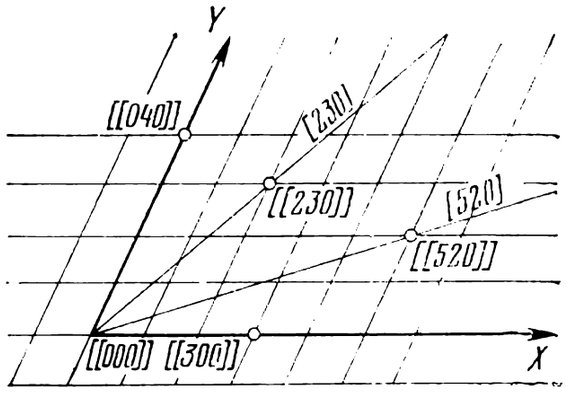


Fig. 1.6. Symbols of lattice points and rows

The lengths of elementary translations, i.e. the edges of a unit cell, are denoted by letters, a, b, c or a_1, a_2, a_3, the angles between them—by Greek letters α, β, γ, (Fig. 1.5).

A *translation group* of a unit cell includes three elementary translations $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ corresponding to three edges of the cell and completely specifying the lattice.*

If three basic translations, $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ are known, the position of any point in the lattice is defined by the vector

$$\boldsymbol{R} = m\boldsymbol{a}_1 + n\boldsymbol{a}_2 + p\boldsymbol{a}_3, \tag{1.1}$$

where m, n, p are integers, while vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ constitute a *vector basis* of the lattice.

Three quantities, m, n, p in double brackets $[[mnp]]$ are called the *symbol of a point.*

Crystallographic direction is the direction of a straight line passing through at least two points of the lattice. An infinite set of lattice points should apparently lie on the same line. One of the points can be taken as the origin of coordinates [[000]]. A crystallographic

* Later (Sec. 9) it will be shown that sometimes it is more convenient to specify a lattice not by a primitive but by a *composite cell* with points not only at the vertices but also in the centre of the cell or in the centres of faces. The translation group will be correspondingly more complicated.

direction (row of a lattice) will be completely specified by its point nearest to the origin.

In distinction from the point symbol [[*mnp*]] the symbol of direction (row of a lattice) is written in ordinary brackets [*mnp*] (Fig. 1.6). Quantities m, n, p are called the *Miller indices* of the given crystallographic direction and all directions parallel to it. Three indices in brackets are called *Miller symbols for the row*. Miller indices are written in succession but read separately, for instance [102]—one, 0, two.

The directions of crystallographic axes of coordinates have Miller indices as follows: axis X—[100], axis Y [010], axis Z—[001], irrespective of the angles between the axes of coordinates. The whole lattice can be obtained by infinite repetitions in space of an elementary parallelepiped by three basic translations.

The quantities a, b, c, α, β, γ or parameters of a crystal (*metrics of a crystal*), are material constants of each crystal substance. In a general case, in crystals $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$, i.e. the basic translations are neither equal to each other, nor orthogonal. All the coordinate systems used in crystallography are listed in Table 4.1.

Space lattices are the natural base of crystallographic coordinate systems. Any of the lattice points is chosen as the origin and three elementary translations intersecting at this point are regarded as three corresponding vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$. These vectors, the so-called *covariant basic vectors*, are known to be non-coplanar, otherwise the volume of a unit cell would be zero. They are the ones that define the crystallographic system of coordinates: their directions coincide with its axes X ($\boldsymbol{a}_1$), Y ($\boldsymbol{a}_2$) and Z ($\boldsymbol{a}_3$), while their lengths represent natural units of measurement along the respective axes. Vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ constitute the right-hand triplet. Correspondingly, the crystallographic system of coordinates XYZ is always rectilinear and right-handed, but in a general case it is oblique-angled, with different scale units along different axes.

The space lattice is a geometric construction, with the aid of which homologous points are determined in crystal space. In other words, the space lattice is a scheme of three-dimensional periodicity of the distribution of particles in crystal structure. The lattice reflects the symmetry of the structure, irrespective of whether a point coincides with an atom of one or another type or situated in an interstice between atoms. In the latter case interstices and the surrounding atoms will be symmetrically repeated in space.

Crystal structure is a concrete array of material particles in space, while symmetry, is the law or principle of this array. The space lattice is the periodicity of repetition in space of individual material particles or groups of these particles, or "vacant spaces" between the particles.

"The lattice is the scaffolding, as it were, upon which the structure is built. It gives us the repeat units, the unit cell, but without defining just what the arrangement of matter is contained in that unit cell. That does not matter at the first stage. The steel scaffolding must come before any consideration of the internal decoration or furniture" (Lonsdale, 1952).

Sec. 2. Crystallographic Projections

The method of crystallographic projections is used for representing the symmetry of external shapes and crystal structures, the anisotropy and symmetry of their properties, and for interpreting X-ray photographs. According to the law of the constancy of angles, the shape of a crystal polyhedron, the symmetry and anisotropy of its

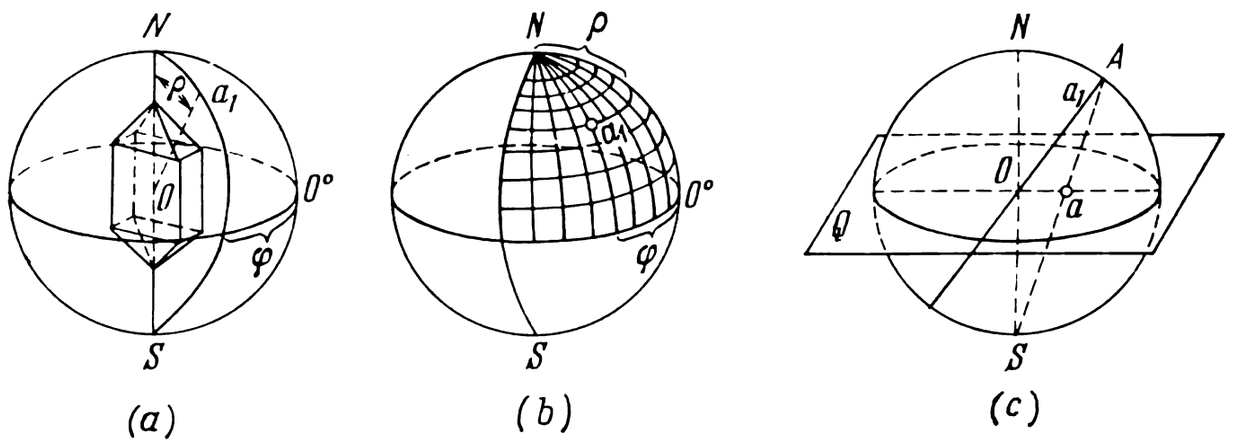


Fig. 2.1. (a) Construction of a spherical projection. (b) The count of coordinates on it. (c) Construction of stereographic projection

properties can be specified by a set of dihedral angles or, as convenient in crystallography, by the angles between perpendiculars to the faces.

Let us imagine a certain sphere surrounding a crystal. From its centre O we draw perpendiculars to the faces of the crystal, extending them until they intersect with the sphere. Each perpendicular will be projected onto the sphere as a "polar point" (point a_1 in Fig. 2.1*a*). Any plane passing through the centre O cuts the sphere along arcs of a circumference. If the projected plane or direction does not pass through point O, it can be shifted parallel to itself without disturbing the angular relations.

The position of any point on the surface of the sphere is defined by two spherical coordinates: ρ is the polar distance reckoned in any direction from zero (north pole N) up to 180° (south pole S), φ is the longitude counted off along the equator from a meridian chosen as the initial one (Fig. 2.1*b*). The resulting spherical projection is in

turn projected on a plane in the form of a stereographic, gnomostereographic or gnomonic projection.

The equatorial plane of the sphere of projections serves as the plane of stereographic and gnomostereographic projections, while the plane of gnomonic projection is tangential to the sphere of projections at the north pole.

In stereographic projection the crystallographic directions are shown as points, the planes as the arcs of great circles. In gnomostereographic projection we have the reverse: planes are shown as points, while the directions as the arcs of great circles.

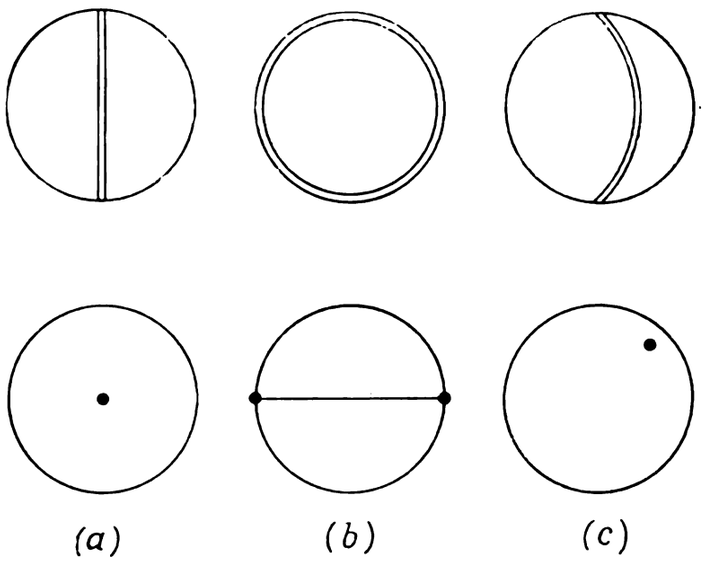


Fig. 2.2. Upper row—stereographic projections of planes (or gnomostereographic projections of directions), lower row—stereographic projections of directions (or gnomostereographic projections of planes), perpendicular (*a*); parallel (*b*); and inclined (*c*) to the plane of projection

The stereographic projection is used mainly for representing the symmetry elements of a crystal as well as the symmetry and anisotropy of its physical properties. Its plane is the equatorial plane Q of the sphere of projections, and the sphere is projected on it as a circle (Fig. 2.1*c*).

In order to project a straight line, for instance OA, a line AS is drawn from polar point A on the sphere of projections to the south pole S of the sphere. Point a of intersection of AS with the circle of projections is the stereographic projection of the direction OA. A stereographic projection of a straight line is a point inside the circle of projections (Fig. 2.2*a*).

Inclined directions that have $0° < \rho < 90°$ are projected inside the circle of projections, the nearer to the outside circumference, the larger is ρ. If $90° < \rho < 270°$, i.e. the direction ends in the lower half of the sphere of projections, in projecting this direction is replaced by an opposite one and is marked on the projection not by a dot but by a cross.

A plane passing through point *O* (crossing the sphere along a circumference (Fig. 2.1)) is shown in stereographic projection as an arc of a great circle. Usually only the intersection of the plane or straight line with the upper hemisphere is projected, to avoid overcrowding the drawing.

Stereographic projections of horizontal planes coincide with the circumference of the circle of projections (Fig. 2.2*b*), those of vertical planes, with the diameters of the circle of projections (Fig. 2.2*a*), while those of inclined planes are shown as arcs resting on the ends of one of the diameters (Fig. 2.2*c*). A vertical line is projected as a point in the centre of the circle of projections, a horizontal line, as two points on the circumference of the equator.

A circumference drawn on the sphere is shown in stereographic projection also as a circumference or a straight line. Angular relations are not distorted in stereographic projection, i.e. the angle between poles of faces on a sphere (measured along the arcs of great circles) is equal to the angle between stereographic projections of the same arcs.

The gnomostereographic projection is used mainly for showing the forms of crystals, their faces and edges, i.e. all the symmetrically equivalent planes and directions. It is also shown as a circle in the equatorial plane of the sphere of projections.

For obtaining the gnomostereographic projection of a crystallographic plane (face), a perpendicular is drawn to this plane (face) up to its intersection with the sphere of projections, next a line is drawn connecting this point of intersection with the south pole of the sphere (or the north pole, when perpendiculars cut the sphere in the lower hemisphere). The gnomostereographic projection of a plane (crystal face) is a point. Projections of perpendiculars to faces above the plane of projection are denoted by small dots, and to those below the plane, by crosses.

Horizontal faces are projected in the centre of the circle of projections (the upper one as a small dot, the lower one as a cross), vertical faces are projected on the circumference of projections itself, while oblique faces are projected inside the circle of projections (Fig. 2.2). The steeper is the obliqueness of a face, the further from the centre will be the point that projects the face. The projections of faces belonging in one zone are arrayed in one great circle of projections.

The gnomostereographic projections of directions (crystal edges) are shown as arcs of great circles. A great circle, i.e. a circle whose centre is the centre of the circle of projections, is the locus of the poles of all faces whose perpendiculars lie in one plane (i.e. in the plane of the great circle).

The stereographic and gnomostereographic projections are often combined in a single drawing.

The solution of problems with the aid of the stereographic and the gnomostereographic projection is done by means of degree grids. The most widely used of these is the Wulff net—a stereographic projection of the whole set of meridians and parallels from the surface of the sphere to the plane of a meridian.

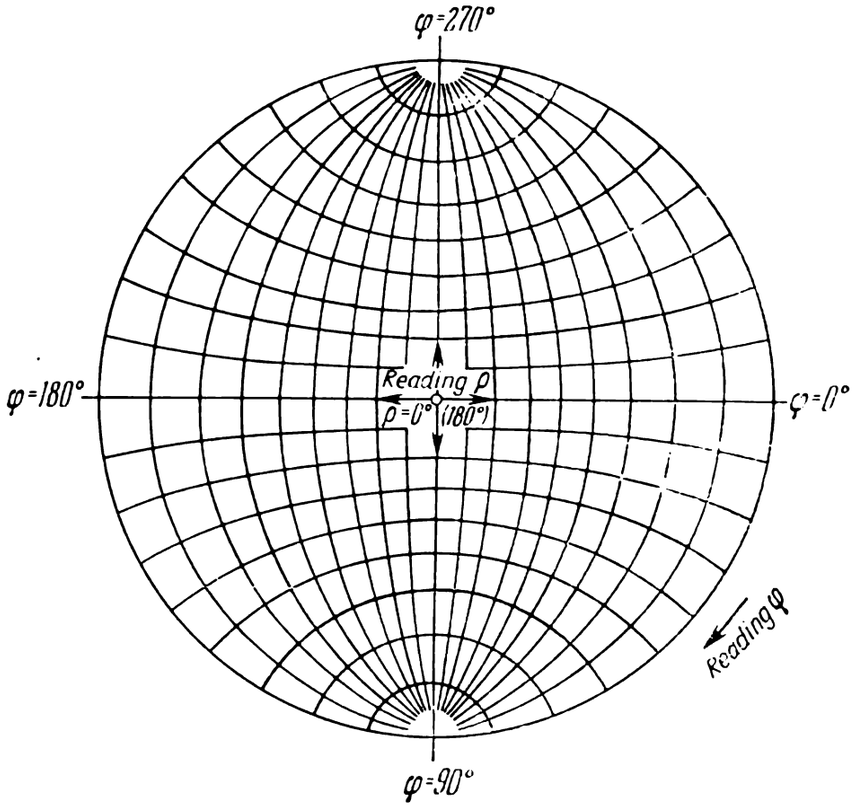


Fig. 2.3. Scheme of the Wulff net and the reckoning of coordinates on it

The Wulff net is usually plotted in a circle of 20 cm in diameter, and the parallels and meridians projected as arcs of a circumference, are drawn through every 2°. The distance between them can be divided visually into four parts more, thus enabling work with an accuracy up to 0.5° (Fig. 2.3).

The position of any point on the Wulff net is defined by its coordinates φ and ρ; polar distances ρ are plotted from the centre of the drawing, longitudes φ—clockwise from the zero meridian along the circumference.

The Boldyrev polar net (Fig. 2.4) is a stereographic projection of a set of parallels and meridians from the surface of a sphere to its equatorial plane. The point of origin is at the south pole. Lines are drawn at every 2° or 5°. Meridians are drawn as straight lines radiating from the centre of the projection; these lines represent arcs of an infinitely large radius. The initial, zero, meridian is marked by 0, other meridians are marked by digits through every 10°. Parallels are drawn as concentric circumferences. The projection of the equator

coincides with the circumference of the projection, the projection of the pole ("zero parallel") with a point in the centre of the projection. Longitudes φ are reckoned from the zero meridian clockwise, polar distances are reckoned from the centre of the projection along the meridian.

The E. S. Fedorov net is a combination of two Wulff nets, rotated by 90° with respect to each other, and the polar net of Boldyrev. It has 5° graduations (Fig. 2.5).

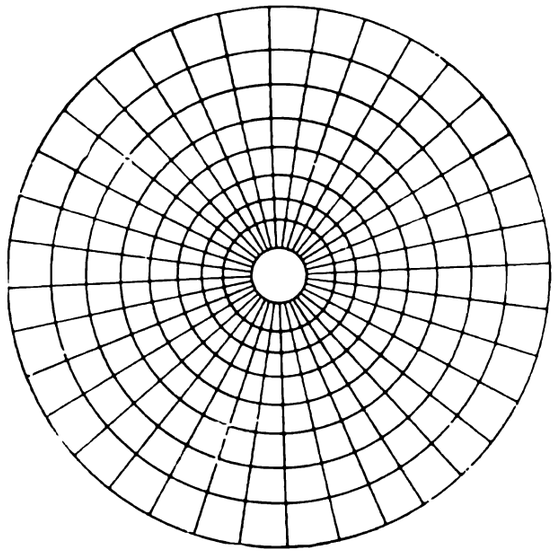


Fig. 2.4. Scheme of the Boldyrev net

In Sec. 24 we shall discuss the use of stereographic projections and Wulff's, Fedorov's, and Boldyrev's nets for representing the symmetry and anisotropy of the physical properties of crystals.

The relation between spherical, stereographic, gnomostereographic and gnomonic projections is shown in Fig. 2.6. The projection of direction *OA* (see Fig. 2.1) produces in the spherical projection of radius *r* a point *a* determined by coordinates φ, ρ in the gnomonic projection (plane *MM*), a point a_2, in the stereographic projection (plane *PP*), a point a_1. In gnomostereographic projection (plane *PP*), the point a_1 is the projection of a plane perpendicular to direction *Oa*. Angular relations in the projections can be seen in Fig. 2.6.

The relations between the three types of projections can be conveniently tabulated as follows:

Type of projection	Representation	
	of a plane	of a straight line
Stereographic	Arc of a great circle	Point
Gnomostereographic	Point	Arc of a great circle
Gnomonic	Point	Straight line

Sec. 3. Simple Finite Elements of the Symmetry of Crystals

Geometric symmetry of a crystal space (or a figure) is the property of the space (or figure) allowing it to coincide with itself by means of certain symmetry transformations. *Symmetric operations*, or *transformations*, are reflections, rotations, translations that result in the space (body) coinciding with itself.

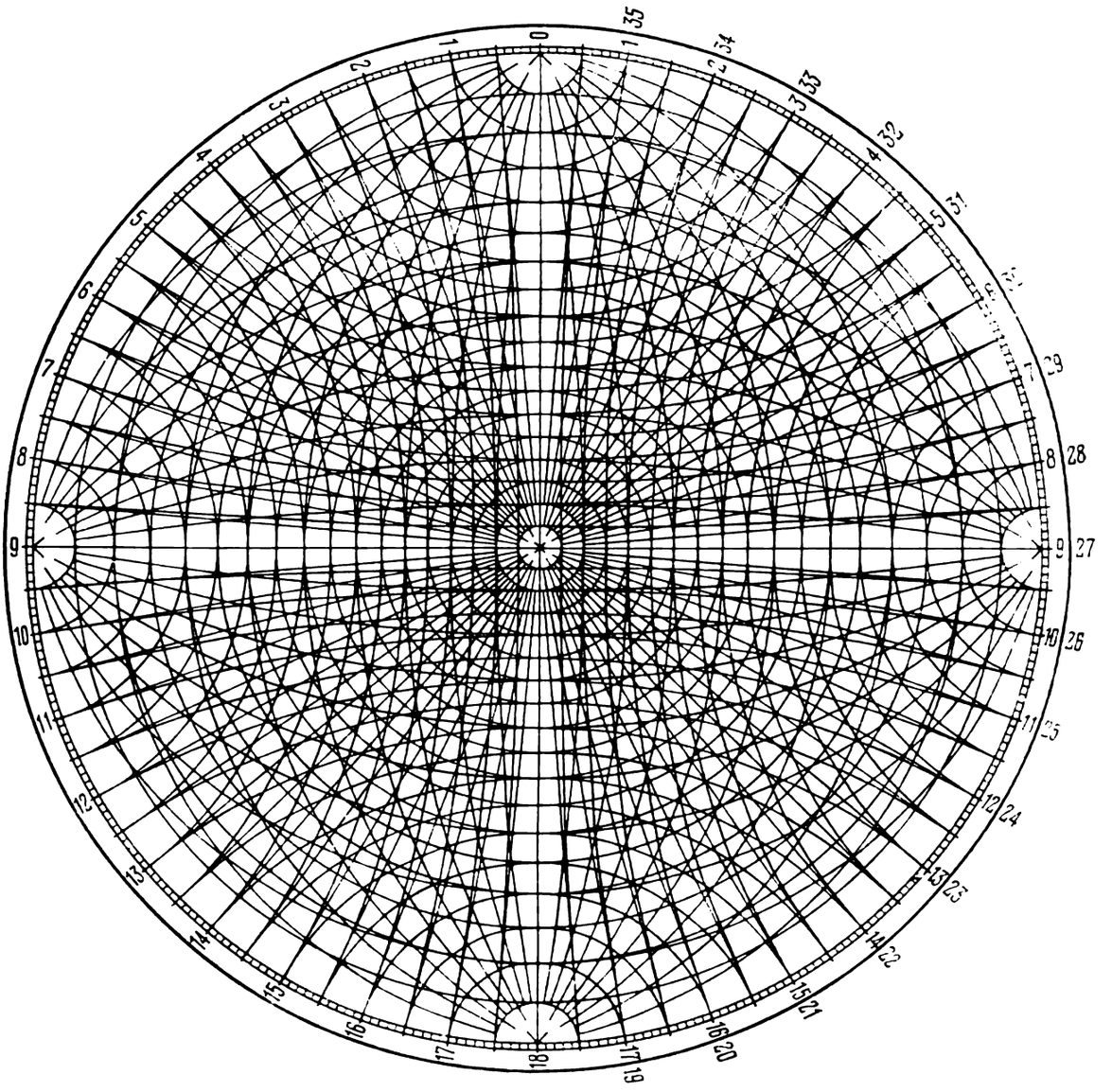


Fig. 2.5. Scheme of the Fedorov net

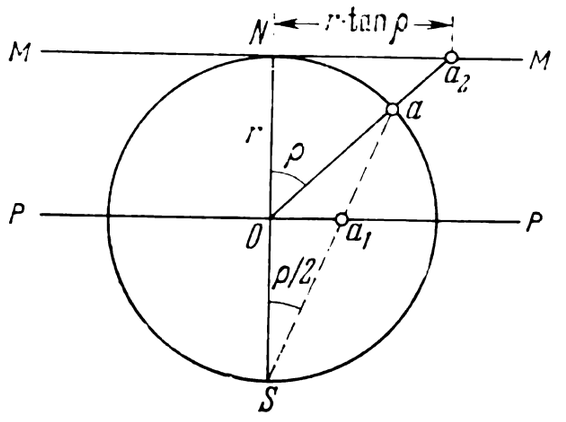


Fig. 2.6. The relationship between spherical, stereographic, gnomostereographic and gnomonic projections

The symmetry and anisotropy of the physical properties of crystals are strikingly displayed in the external polyhedral forms of crystals. It should be noted that the form of a real crystal polyhedron is always the result of not only the anisotropy of the rates of growth, but also of the external conditions under which the crystal grew, such as the temperature gradient, contact with adjacent crystals or the crystallizer walls, the effect of gravity, of non-homogeneity of the environment, etc. Leaving aside the real growth conditions, we shall now discuss the symmetry of ideal crystal polyhedrons.

A symmetrical body or a *symmetrical polyhedron* is a body (polyhedron) which can coincide with itself as the result of symmetric transformations.

Elements of symmetry are the auxiliary images (points, straight lines, planes) with the aid of which the symmetry of a body (or space) is revealed. In all symmetric transformations the distances between the points of a body remain unchanged, i.e. no extension, compression, bending, etc. occur.

Symmetric transformations can be divided into two types: (1) *finite*, or *point* ones in which at least one point of a body remains in its place, and (2) *infinite*, or *space* ones in which not a single point of a body remains unmoved. Finite symmetric transformations correspond to the symmetry of ideal crystal polyhedrons; the infinite ones, to the symmetry of structures.

For specifying symmetry elements we shall use international symbols drawn up by Hermann and Mauguin and adopted by the International Union of Crystallography (International Tables). In physical and crystallographic literature other notation systems are often used; they will be explained later.

We shall use the stereographic projection for showing symmetry elements and symmetric transformations. International symbols for showing symmetry elements on the projection planes are given in Table 3.1.

Simple Finite Symmetry Operations. Simple symmetry operations are reflections and rotations. They are specified by the following symmetry elements:

	International symbol
Plane of symmetry	m
Axis of symmetry	n ($n = 2, 3, 4, 6$)
Centre of symmetry	$\bar{1}$

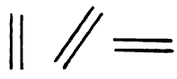
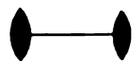
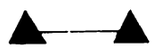
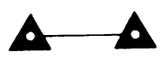
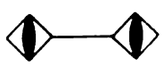
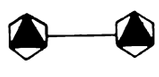
(Here n is the order of the axes, i.e. 1-fold, 2-fold, 3-fold, 4-fold, 6-fold, see later).

A symmetry plane (m) is the plane which divides a figure into two mirror-equivalent parts, located with respect to each other as an object and its reflection in a mirror, as the right and the left hands.

For example, an equilateral triangle has three symmetry planes

Table 3.1

Symmetry Elements of Finite Figures and Their Standard Notation

Description			International notation	Representation with respect to the plane of drawing	
				perpendicular	parallel
Symmetry plane			*m*		
Centre of symmetry			$\bar{1}$		
Symmetry axes	rotation	two-fold	2		
		three-fold	3		
		four-fold	4		
		six-fold	6		
	inversion	three-fold	$\bar{3}$		
		four-fold	$\bar{4}$		
		six-fold	$\bar{6}$		

perpendicular to the plane of the triangle; their projections on the triangle plane are shown in Fig. 3.1. If the symmetry of an ordinary triangle, i.e. of a geometric figure consisting of three mathematical straight lines is discussed, it has no other symmetry planes. But if the triangle under consideration is a material figure, its symmetry can be more complicated. If a triangle is cut out of white paper so that its face and back sides are similar, it will have another plane of

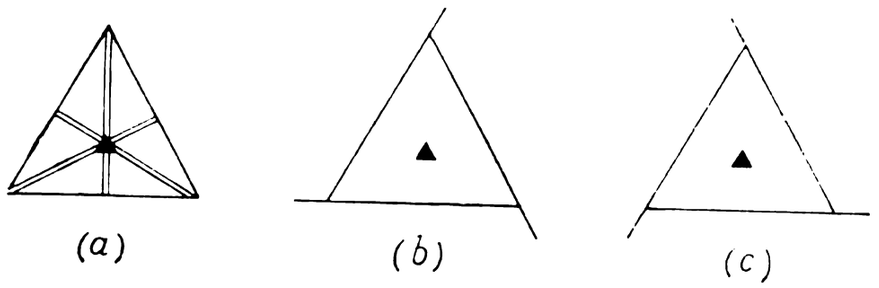


Fig. 3.1. Symmetry of a triangle: (a) neutral 3-fold axis and three symmetry planes. (b) right-hand 3-fold axis, no symmetry planes. (c) left-hand 3-fold axis, no symmetry planes

symmetry coinciding with the plane of the triangle itself. But if the triangle "face" and "back" sides are different, e.g. if it is white on one side and black on the other, it will have no such symmetry plane.

9 symmetry planes can be counted for a cube (Fig. 3.2), three of which are perpendicular to the cube faces and six pass along diagonal

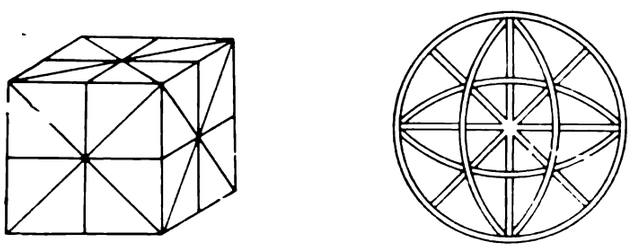


Fig. 3.2. Three coordinate and six diagonal planes of the cube symmetry

planes. On the right hand of Fig. 3.2 the stereographic projection of the symmetry planes of a cube is shown.

The axis of symmetry (n) is a straight line; rotation about it superposes a figure on itself. The elementary angle of rotation, i.e. the smallest of the angles of rotation superposing the figure upon itself, is a divisor of the angle 2π; viz., it is contained a whole number of times in 2π, otherwise the figure would not coincide with itself after a complete revolution. The number n is the so-called *order of an axis*, it gives the number of times that the figure superposes on itself during a complete revolution about the axis.

Fig. 3.1. shows three equilateral triangles. Each of them has a 3-fold symmetry axis. Moreover, the first triangle (a) has three symmetry

planes (perpendicular to the plane of the drawing), while the second and third triangles (*b*) and (*c*) have no symmetry planes, but only right- or left-hand symmetry axes, respectively. Discussing the triangles as material figures we can describe them as symmetrical right- or left-hand triangles.

Any figure, geometrical or material, has a one-fold symmetry axis: any body rotated through 360° about any direction completely superposes on itself.

The most symmetric geometric body is a sphere: each of the infinite number of its diameters is an infinite-fold (∞) symmetry axis; an infinite number of symmetry planes passes, in turn, through each diameter.

A circular cone has one infinite-fold symmetry axis which coincides with the cone axis. The cone superposes on itself when rotated

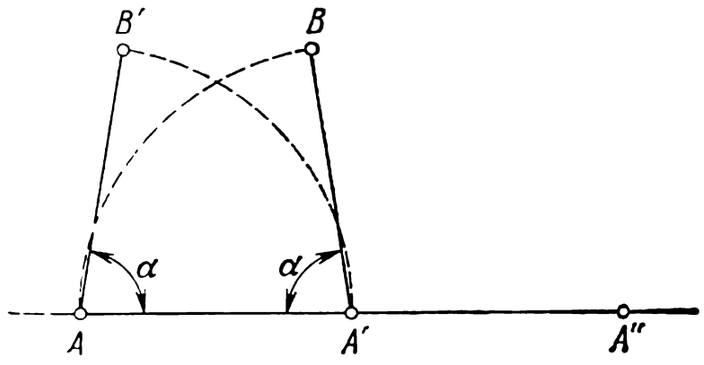


Fig. 3.3. To the proof of the impossibility of a 5-fold symmetry axis in a crystal medium

through any angle about this axis. Moreover, any plane passing through this axis serves as a symmetry plane for this cone; thus the cone has an infinite number of symmetry planes passing through its axis.

Let us again change over from a geometric body to a material one. For example, let the cone be hatched or covered with velvet whose pile hairs are all brushed to one side, or, this being the simplest case, let the cone rotate uniformly about its axis. The cone will as before coincide with itself in rotation about its axis through any angle, i.e. it will still have a symmetry axis, but all symmetry planes will disappear: the uniform rotation changes the symmetry of the material figure.

1- to ∞-fold symmetry axes can be found in natural objects—in flowers, fruits, shells, etc., in geometric figures, in works of art. In geometric crystal forms only 1-, 2-, 3-, 4-, 6-fold symmetry axes are possible. Neither 5-fold axes, nor those higher than 6-fold are possible.

Let us imagine that an n-fold symmetry axis with an angle of rotation $\alpha = 2\pi/n$ is perpendicular to the plane of the drawing

at point A which is a point in the A, A', A'', . . . row, shown in Fig. 3.3. A similar axis will obviously appear at each homologous point of the row. If rotation through angle α about the axis at point A will transfer point A' to position B', a similar rotation about the axis at point A' will transfer point A to position B. Points B, B', etc. should form a row of homologous points parallel to the AA' row, i.e.

$$BB' = Nt$$

where t is the translation (distance) AA', and N is an integer. Since $BB' = t - 2t \cos \alpha$, then

$$t - 2t \cos \alpha = Nt,$$

hence

$$\cos \alpha = \frac{1-N}{2}.$$

From condition

$$-1 \leqslant \cos \alpha \leqslant +1$$

we find all the possible values of the order of the axes:

N	-1	0	1	2	3
$\cos \alpha$	1	1/2	0	$-1/2$	-1
α	0°	60°	90°	120°	180°
Symmetry axis	1-fold	6-fold	4-fold	3-fold	2-fold

Thus, only 2-, 3-, 4-, and 6-fold axes satisfy the requirement of the periodicity and continuity of the row of homologous points.

It can be similarly proved that only the same symmetry axes can exist in a plane net and a space lattice. 5-fold, 7-fold and higher-fold symmetry axes are impossible in crystals.

It is interesting to note that a 5-fold axis, not to be found in any crystal, has been encountered in biological structures ("crystals of living nature") studied within recent years. "One can think,—writes academician N. V. Belov,— that a five-fold axis is a peculiar instrument of small organisms in their struggle for survival, an insurance against petrification, against crystallization, the first step of which would be their "capture" by a lattice" (Belov, 1962).

When discussing the symmetry of a body, it is necessary to draw a clear distinction between the symmetry of the body alone, without taking account of its environment, or of the symmetry of the body and its environment. The shapes of real crystal polyhedrons always bear imprints of their growth conditions and of the symmetry of the crystal-forming environment. However, in this book we discuss the symmetry of an ideal crystal polyhedron without taking account of its environment.

In a geometric body there can be several symmetry axes of different orders along with the symmetry planes and other symmetry elements. For instance, a cube has three 4-fold axes (they pass through the

centres of faces as axes of a rectangular coordinate system), four 3-fold axes (through pairs of opposite vertices) and six 2-fold axes (through the centres of opposite edges).

Let us discuss two points on a projection (Fig. 3.4). Point *B* can be obtained by symmetric transformation from point *A* upon reflection of the latter in the symmetry plane *m* (Fig. 3.4*a*) or upon its rotation about the 2-fold symmetry axis in the plane of projection (Fig. 3.4*b*). How are we to know what transformation has actually occurred? The difference would be apparent, if not a point but a material figure were symmetrically rotated or reflected: a triangle with its front white and its back black. The 2-fold axis (Fig. 3.4*b*) rotates the triangle "from its face to its back", while the symmetry plane (Fig. 3.4*a*) reflects it without rotation. If the triangle is reflected in the symmetry plane *m* which coincides with the plane of the paper, the black side will coincide with the white one; we show it by a black dot on white background (Fig. 3.4*c*)*.

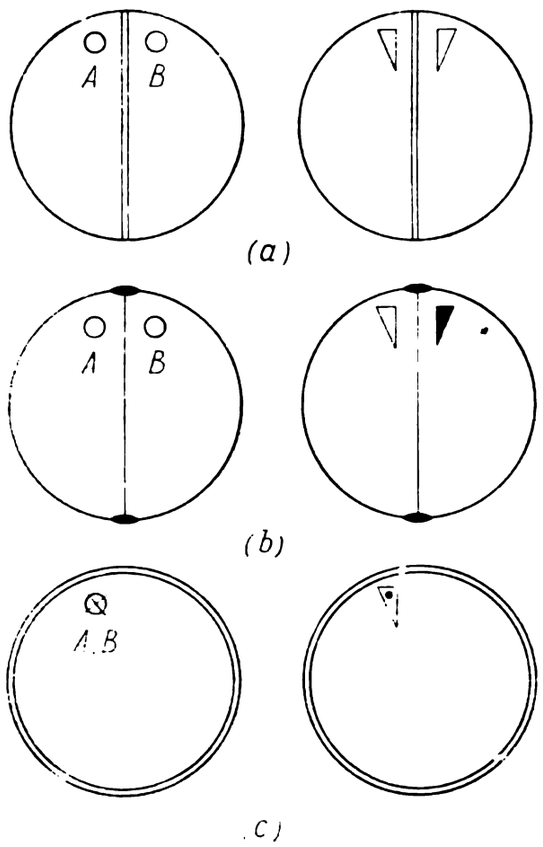


Fig. 3.4. A point (on the left) and a material triangle, with a face (white) and back (black) sides (on the right) are symmetrically transformed by a symmetry plane perpendicular to the plane of the paper (a); by a 2-fold axis in the plane of the paper (b); by a plane of symmetry coinciding with the plane of the paper (c)

A centre of symmetry (1) (*centre of inversion*, *centre of reciprocal equality*) is a singular point within a figure; its characteristic feature is that any straight line drawn through it will run into similar (opposite) points of the figure on either side of and at equal distances from the centre. Thus, a symmetric transformation at the centre of symmetry is the reflection in a point that turns the figure "back to front" (Fig. 3.5*a*).

Fig. 3.5*b* shows stereographic projections of two crystal faces symmetric with respect to the centre of symmetry, one face is in

* "A white triangle in the front hemisphere having been reflected in the symmetry plane passes to the back side of the sphere and is positioned just under it, so that it cannot be seen. Having made a hole in the white triangle, we shall see the second one through it, and this second triangle will appear black. This is the meaning of the black dot in the centre of the triangle" (Shubnikov, 1951).

the upper half of the sphere of projections (dot), the second one is in the lower half (cross). The same transformation is shown with the aid of a black-white triangle: reflection at the centre of symmetry turns the triangle "back to front".

Crystals with a centre of symmetry can have no polar straight lines. A straight line whose properties differ in the two opposite directions is called *polar* (Fig. 3.5*c*). Let us discuss, for instance, a 4-fold symmetry axis in a tetrahedral prism or in a tetrahedral pyramid. Two bases of the prism are congruent; when reflected in the centre of symmetry or in a transversal plane of symmetry, one end of a 4-fold axis will coincide with the other and vice versa; there are no differences in the directions of the 4-fold axis—the axis is *not polar*. The pyramid also has a 4-fold axis, but no symmetry operations inherent in the pyramid itself can match its apex with its base, i.e. one end of the axis with the other—the 4-fold symmetry axis of the pyramid is polar. However, 4-fold axes of a cube are not polar because the cube possesses a centre of symmetry. The symmetry axis of a circular cone is polar, that of a circular cylinder is not. For details see Appendix C.

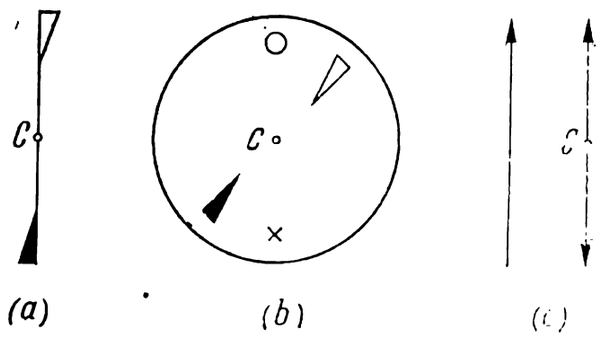


Fig. 3.5. Symmetric transformation by a centre of symmetry (a); stereographic projection of faces symmetric with respect to the centre of symmetry (b); a polar arrow (without a centre of symmetry) and a non-polar (centrosymmetric) one (c)

Thus all the possible simple symmetry elements in crystals are confined to planes, axes, and centre of symmetry (m, 2, 3, 4, 6, $\bar{1}$).

Each symmetry element of a figure generates a certain combination of symmetry operations: a 3-fold axis produces rotations of the figure through 120° and 240°; a 4-fold axis, through 90°, 180°, 270°; a 6-fold axis, through 60°, 120°, 180°, 240°, 300°. All rotations generated by a symmetry axis can be regarded as a result of the repetition of one elementary rotation; for a 2-fold axis it is the rotation through 180°, for a 3-fold axis, through 120°, for a 4-fold axis, through 90°, for a 6-fold axis, through 60°. In distinction from symmetry axes, denoted by ordinary digits, the elementary rotations will be denoted by the axis symbols in italics, with an index showing which of the given symmetry axis coincides with a particular coordinate axis: 2_x, 3_z, etc. On the basis of crystallographic indices this will be written as $2_{[100]}$, $3_{[001]}$, etc. The result of the repetition of several elementary rotations will be regarded as a corresponding power of an elementary rotation; if, for example, the rotation through 60° is denoted by 6_z, the rotations about the same axis through 120°, 180°, 240°, 300°

will be designated respectively as 6_z^2, 6_z^3, 6_z^4, 6_z^5. Obviously, the following relations will hold

$$6_z^2 = 3_z; \quad 6_z^3 = 2_z; \quad 4_z^2 = 2_z.$$

The operation of reflection in the symmetry plane m is denoted by the symbol of the plane with an index showing a coordinate axis particular to the plane: m_x or $m_{(100)}$.

The operation of inversion, i.e. the reflection in the centre of symmetry $\bar{1}$, is denoted by symbol $\bar{1}$.

Besides this, the symmetry operations also include *identification*, or a *unit operation*, which is "the operation of transformation of

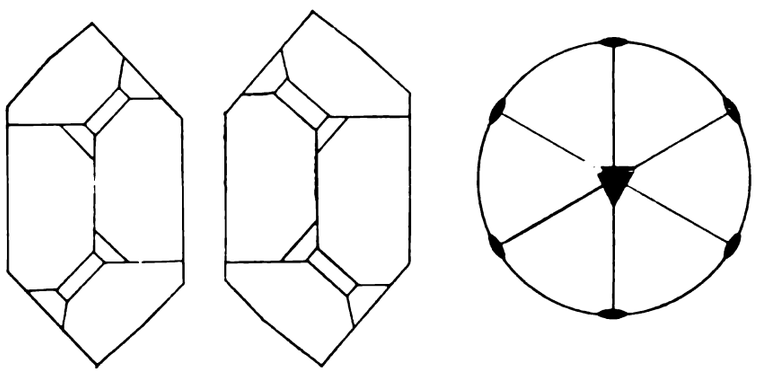


Fig. 3.6. Right- and left-hand quartz crystal and a stereographic projection of its symmetry elements

a figure into itself by leaving it unmoved"*. It is denoted by symbol 1.

If a figure has several symmetry elements, the set of symmetry operations generated by all of them together will accordingly become more and more complicated.

Let us discuss an example. Let a solid have a 3-fold axis and a 2-fold axis perpendicular to it (this is the symmetry of quartz crystals, Fig. 3.6). The 3-fold axis generates rotations 3 and 3^2, while the 2-fold axis produces rotation 2_x. Since each symmetry operation transforms the body (an ideal quartz polyhedron) into itself, the result of several consecutive symmetry operations, called the *product* of these operations, will also transform the solid into itself and thus will also be one of the symmetry operations. Let us discuss the result of two consecutive symmetry operations: first 3_z, then 2_x. In projection (Fig. 3.7*a*) the same result will be obtained upon a single operation, i.e. 2_u. In Fig. 3.7*a* triangle A is brought to position B by rotation through 120° about the axis 3_z and then to position C by rotation through 180° about the axis 2_x. However, A can be brought

* (Shubnikov, 1951). The term "identification" was also suggested by Shubnikov.

to C at once by rotation about the axis 2_u. This can be written as $2_x 3_z = 2_u$. The operation that is done first is written on the right. The order of writing down the operations is important: it can be seen from Fig. 3.7*b* that a change in the order of the operations produces a different result: $3_z 2_x = 2_y$. Indeed, in Fig. 3.7*b* the triangle A is brought to position D by rotation through 180° about the axis 2_x,

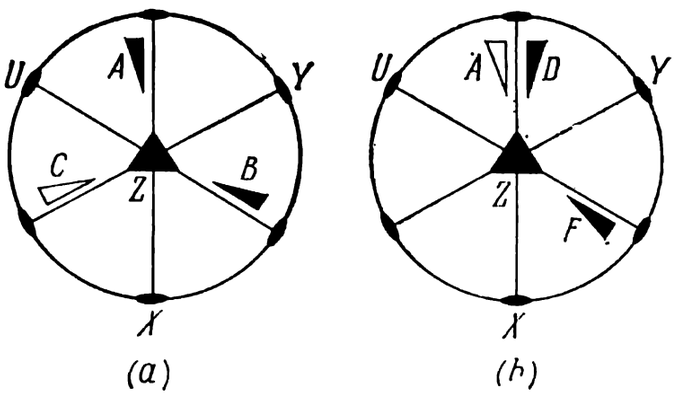


Fig. 3.7. The result of two consecutive symmetry operations: (a) $2_x 3_z = 2_u$, (b) $3_z 2_x = 2_y$

and then to position F by rotation through 120° about the axis 3_z; A also can directly be brought to F by rotation through 180° about the axis 2_y.

The results of all possible pairs of consecutive symmetry operations are collected in a multiplication table (the one below is for group 32 as will be explained in Sec. 5).

Factors		Written on the right					
		1	3_z	3_z^2	2_x	2_y	2_u
Written on the left	1	1	3_z	3_z^2	2_x	2_y	2_u
	3_z	3_z	3_z^2	1	2_y	2_u	2_x
	3_z^2	3_z^2	1	3_z	2_u	2_x	2_y
	2_x	2_x	2_u	2_y	1	3_z^2	3_z
	2_y	2_y	2_x	2_u	3_z	1	3_z^2
	2_u	2_u	2_y	2_x	3_z^2	3_z	1

As can be seen from the Table, the availability of 3_z and 2_x axes in a quartz crystal produces two more symmetry elements in it: the axes 2_y and 2_u. Thus, if a 2-fold axis is perpendicular to a 3-fold axis, there will be on the whole three 2-fold axes perpendicular to the 3-fold axis. Theorem 1 for the multiplication of symmetry operations is derived from this particular example:

Theorem 1. If a 2-fold symmetry axis is perpendicular to an n-fold symmetry axis, there would be on the whole n 2-fold axes perpendicular to the n-fold axis. The combination of the n-fold symmetry axis with the 2-fold symmetry axis perpendicular to it is denoted $n2$; in this case we have combination 32 (see Fig. 3.6).

Let us formulate some more theorems on the multiplication of symmetry operations which will subsequently be used in this book. We give here only some illustrative explanatory examples, while strict analytical proofs are given in Appendix D.

Theorem 2. The line of intersection of two symmetry planes is always a symmetry axis with an angle of rotation twice as large as

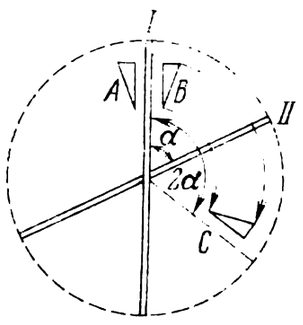


Fig. 3.8. Reflection in two intersecting symmetry planes is equivalent to rotation about a symmetry axis

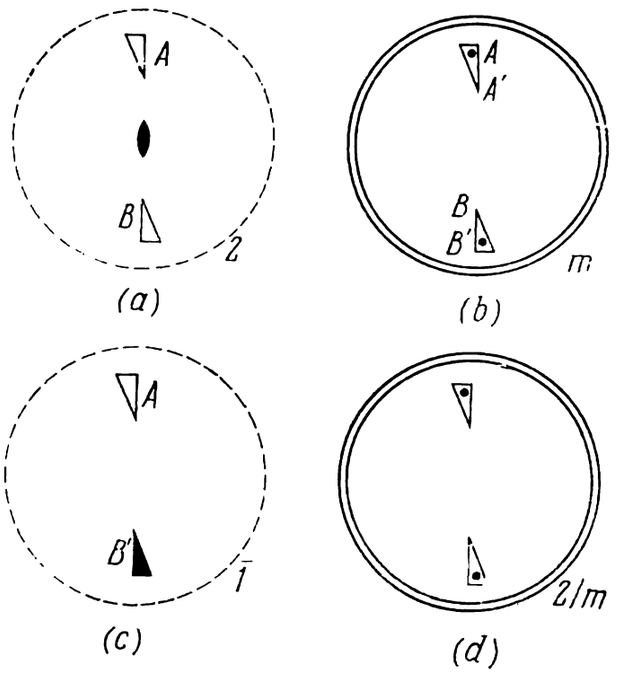


Fig. 3.9. An even-fold symmetry axis and a plane perpendicular to it generate a centre of symmetry

the angle between the planes. For explanation see Fig. 3.8. Reflection in plane I moves triangle A to position B while that in plane II moves the triangle from B to C. But the transfer from A to C can also be accomplished by rotation through an angle 2α about an n-fold axis, i.e. $m_{II} \cdot m_{I} = n_{2\alpha}$.

Theorem 2a (converse of Theorem 2). Two reflections in symmetry can be substituted for the rotation about a symmetry axis. One plane is then drawn arbitrarily through the axis, while the second one should form an angle with the first plane equal to half the angle of rotation about the axis in the direction of the rotation. Fig. 3.8 proves the case again.

Theorem 3. The intersection point of an even-fold symmetry axis with a symmetry plane perpendicular to it is the centre of symmetry. In Fig. 3.9 the 2_z axis perpendicular to plane m_z transfers triangle A

to position B (Fig. 3.9*a*), the plane giving the reflections A-A', B-B' (Fig. 3.9*b*), but A and B' as well as A' and B are also connected by a generated centre of symmetry (Fig. 3.9*c*).

The combination of an n-fold symmetry axis and a symmetry plane perpendicular to it is denoted n/m, in this case, a combination $2/m$ (Fig. 3.9*d*).

The following theorems are proved similarly.

Theorem 3a. If an even-fold symmetry axis has a centre of symmetry, there will be a symmetry plane perpendicular to the axis.

Theorem 3b. If a symmetry plane passes through the centre of symmetry, there will be an even-fold symmetry axis passing through the centre perpendicular to the plane.

Theorem 4. If a symmetry plane passes through an n-fold symmetry axis, there will be n such planes; this combination is denoted nm. The theorem is proved in the same way as theorem 1, see Fig. 3.8.

Upon mutual multiplication of symmetry operations we obtain those already listed and still another, a new one: the product of an elementary rotation n and inversion $\bar{1}$ made in any sequence is a symmetry operation called an *elementary inversion rotation* $\bar{n}$ i.e. $\bar{1}\cdot n = n\cdot\bar{1} = \bar{n}$.

The axis about which the inversion rotations are performed is called an *inversion symmetry axis.* The inversion axes in crystals can be only 1-, 2-, 3-, 4- and 6-fold, as is the case with rotation axes.

Two of the operations listed above belong to the elementary inversion rotations: the action of a 1-fold axis is equivalent to the action of the centre of symmetry, while an inversion rotation about a $\bar{2}$-fold axis is equivalent to the action of a symmetry plane: $\bar{2} \equiv m$. Other inversion rotations are new ones.

The repetition of elementary inversion rotations gives the following results:

$$\bar{3}_z^2 = 3_z; \quad \bar{3}_z^3 = \bar{1}; \quad \bar{3}_z^4 = 3_z;$$

$$\bar{4}_z; \quad \bar{4}_z^2 = 2_z; \quad \bar{4}_z^3; \quad \bar{4}_z^4 = 1.$$

For instance, inversion rotation about a $\bar{3}$-fold axis perpendicular to a plane (Fig. 3.10*a*), i.e. rotation through 120° with simultaneous reflection in the centre of symmetry brings triangle (or point) A to position B, then to position C, and so on. Similarly, in Fig. 3.10*b* triangle (or point) A is brought to B, then to C and so on, by rotation through 90° with simultaneous reflection in the centre ($\bar{4}$-fold axis).

The symmetry of crystal polyhedrons is sometimes shown by still another symmetry operation—*mirror rotation* which represents rotation about a symmetry axis along with a reflection in a plane perpendicular to the axis. Mirror-rotation axes Λ_1, Λ_2, Λ_3, Λ_4, Λ_6 are equivalent to inversion symmetry axes: $\Lambda_1 =$

$= \bar{2} = 4_2 = m$, $\Lambda_2 = \bar{1}$, $\Lambda_3 = \bar{6}$, $\Lambda_4 = \bar{4}$, $\Lambda_6 = \bar{3}$. Attention should be paid to the fact that Λ_6 is identical with $\bar{3}$ and not with $\bar{6}$, while Λ_3 is in turn identical with $\bar{6}$ and not with $\bar{3}$. The same relates to the axes $\Lambda_1 \equiv \bar{2}$ and $\Lambda_2 \equiv \bar{1}$.

The inversion rotation is both a rotation about the symmetry axis and reflection in the centre of symmetry performed *simultaneously*; these two operations cannot be separated, therefore the availability

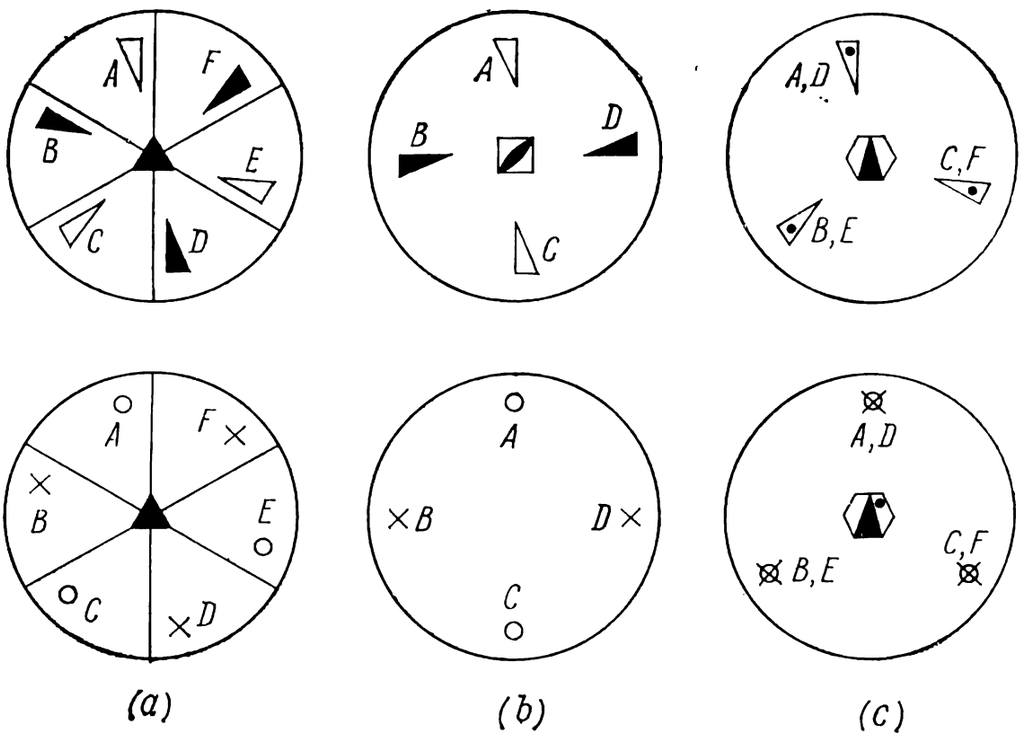


Fig. 3.10. Symmetric transformations by inversion symmetry axes: by a $\bar{3}$-fold axis (a); by a $\bar{4}$-fold axis (b); by a $\bar{6}$-fold axis (c) of a material triangle (upper row) or of a point in standard representation in stereographic projection (lower row)

of an inversion symmetry axis in a crystal does not mean that the crystal has a centre of symmetry, neither is it at variance with the presence of polar directions (as is well known, the inversion axis itself is non-polar!).

So, *the symmetry of crystal polyhedrons is completely specified by the set of symmetry elements* m, 1, 2, 3, 4, 6, $\bar{3}$, $\bar{4}$, $\bar{6}$. Now we shall return to the theorems concerning their multiplication.

Theorem 5 (Euler's theorem). The resultant of two intersecting symmetry axes is a third axis passing through the point of their intersection.

Fig. 3.11 illustrates the theorem. Axis 4_z transfers $A \rightarrow B$, axis 2_x transfers B to C, but A can be transferred to C directly by rotation about axis 2_{xy}, i.e.

$$2_x \cdot 4_z = 2_{xy}.$$

These transformations could be conducted in another sequence:

operation	2_x	transfers	$A \to B$
"	4_z	"	$B \to C$
"	$2_{\bar{x}y}$	"	$A \to C$

i.e.

$$4_z \cdot 2_x = 2_{\bar{x}y}.$$

Let us illustrate Euler's theorem with the aid of projection. of Fig. 3.12 A and B are the traces of symmetry axes with angles In

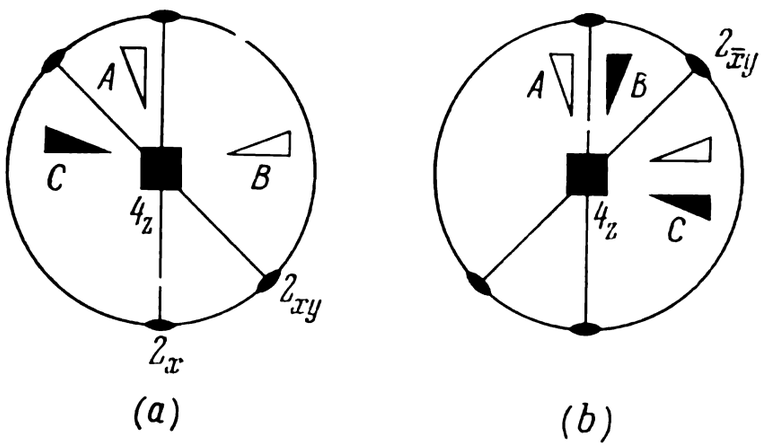


Fig. 3.11. On Euler's theorem: (a) $2_x \cdot 4_z = 2_{xy}$, (b) $4_z \cdot 2_x = 2_{\bar{x}y}$

rotation $\alpha = 2\pi/n$ and $\beta = 2\pi/m$, respectively. From the intersection point of these axes, as from a centre, we describe a sphere and project it on the plane of the paper, having turned it so as to make axis A emerge from the centre of the circle of projections. According to the Theorem 2a, rotation about axis A can be represented as two reflections in symmetry planes, the first of the planes being drawn arbitrarily, while the second one should make an angle $\alpha/2$ with it; we draw the first plane through axis B. We shall similarly replace rotation about axis B by two reflections in planes intersecting at an angle $\beta/2$, the first plane being drawn through A. The product

$$m_{\mathrm{I}} \cdot m_{\mathrm{I}} = 1,$$

i.e. the result of two consecutive reflections in the same plane leaves the figure in place. There remain two planes m_{II} and m_{II} intersecting at angle $\gamma/2$ and, according to Theorem 2, equivalent to symmetry axis C with the angle of rotation $\gamma = 2\pi/p$. The theorem is proved.

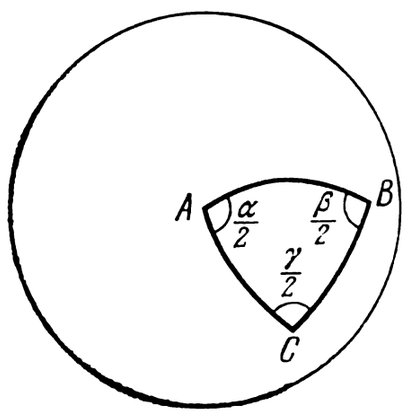


Fig. 3.12. Illustrating Euler's theorem with the aid of stereographic projection

It has been shown earlier that symmetry axes in a crystal can only be 2-fold, 3-fold, 4-fold, 6-fold axes. What combinations of the axes are possible in a crystal?

Having performed all possible rotations A, A^2, A^3, . . ., B, B^2, B^3, . . . and so on about axes A, B, C in Fig. 3.12, we shall obviously obtain n emergences of axis A on the sphere, m emergences of axis B and p emergences of axis C; drawing symmetry planes between them, which appear on the sphere as arcs of great circles, we obtain a net of spherical triangles on the surface of the sphere. It is known from spherical trigonometry that the sum of the angles of a spherical triangle S is

$$180^\circ < S \leqslant 3 \cdot 180^\circ.$$

On the other hand, from the condition of axes A, B, C being only 2-fold, 3-fold, 4-fold, 6-fold, it follows that angles between the sides of triangles can only be 90°, 60°, 45°, 30°. Therefore, only the combinations of symmetry axes listed below can be stable:

Angles	Sums of angles	Combinations of axes	Crystallographic system
90° 90° 90°	270°	2, 2, 2	Rhombohedral
60° 90° 90°	240°	3, 2, 2	Trigonal
45° 90° 90°	225°	4, 2, 2	Tetragonal
30° 180° 180°	390°	6, 2, 2	Hexagonal
60° 60° 90°	210°	3, 3, 2	Cubic
45° 60° 90°	195°	4, 3, 2	

The last column contains the names of crystallographic systems which are explained in the following section.

Sec. 4. Crystallographic Categories and Systems

On the basis of their geometric symmetry, forms of growth and the symmetry of physical properties, crystals are divided into categories and systems.

Before becoming acquainted with categories, we want to introduce the idea of singular directions in a crystal. The only non-repetitive direction in a crystal is called a *singular* or *unique* one*. For instance, a six-fold axis in a snowflake, a four-fold axis in a tetragonal pyramid or a six-fold axis in a hexagonal pencil are singular directions: no other symmetry elements of these polyhedrons can be

* This relates not only to a crystal, but to any symmetric polyhedron.

repeated so that another four-fold axis or a second six-fold axis could be produced.

A cube has more than one 4-fold axis, there are three of them and each can be matched with any other such axis, for example, by reflection in any of the six diagonal planes of the cube symmetry. Not only the symmetry axes, but any direction in a cube will be unfailingly repeated symmetrically, since a cube has no singular directions. The repeating directions in a crystal that are interconnected by symmetry elements are called *symmetrically equivalent*.

Depending on the number of singular (unique) directions and on the available symmetry axes, crystals are divided into three categories:

higher category—crystals have no singular directions, but have several symmetry axes greater than 2-fold (for example, a cube);

intermediate category—crystals have one singular direction coinciding with the only symmetry axis, 3-, 4-, or 6-fold one, i.e. higher than 2-fold (example, trigonal, tetragonal and hexagonal prisms);

lower category includes crystals with several singular directions and only 2-fold axes (example, a so-called rhombic prism (a brick) with three 2-fold axes).

The higher category includes crystals with several symmetry axes higher than 2-fold; there are always four 3-fold axes and, moreover, there can be three 4-fold or $\bar{4}$-fold inversion axes.These are highly symmetrical crystals with no singular directions. To any direction in a crystal of the higher category there correspond other symmetrically equivalent directions. The properties of a crystal in symmetrically equivalent directions should be similar, therefore in crystals of the higher category the anisotropy of their properties is the least marked. The physical properties of crystals, described by a second-rank tensor (see Ch. III), in other words, electrical conductivity, thermal conductivity, dielectric permittivity, etc. are isotropic, isometric in such crystals.

The intermediate category includes crystals that have one singular direction, i.e. a 3-, 4- or 6-fold symmetry axis (a rotation or an inversion one). The anisotropy of the physical properties of these crystals is much more marked than of those in the higher category.

Crystals of the lower category have only 2-fold symmetry axes and several singular directions. There are the least symmetric crystals and their physical properties are the most anisotropic.

The three categories are in turn divided into seven systems, according to their characteristic symmetry and to the combinations of symmetry axes (see Sec. 3).

The lower category is divided into three systems*:

* Crystallographic terms are formed mostly from a few Greek words: *mono*—1, *di*—2, *tri*—3, *tetra*—4, *penta*—5, *hexa*—6, *hepta*—7, *octa*—8, *deca*—10, *dodeca*—12, *hedra*—face, *gonia*—angle, *pinax*—board, *clino*—incline, *scalena*—oblique, unequal, *trapeza*—table, *sin*—similar.

Table 4.1

Division of Crystals into Categories and Systems

Category	Number of singular directions	Division into: 6 systems	Division into: 7 systems	Characteristic symmetry	Form of unit cell	Coordinate axes	Conventional array of axes	Parameters characteristic of substance
		Triclinic	Triclinic	None	Oblique-angled parallelepiped	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$	Along crystal edges; $c < b < a$	$a : b : c$, α, β, γ
Lower	Several	Monoclinic	Monoclinic	2-fold axis or symmetry plane	Right prism with parallelogram base	$a \neq b \neq c$, $\alpha = \gamma = 90° \neq \beta$	1. Axis Y along 2-fold axis or perpendicular to plane m 2. Axis Z along 2-fold axis or perpendicular to m; $c < b < a$	$a : b : c$, β $a : b : c$, γ
		Rhombic	Rhombic	Three 2-fold axes or three symmetry planes	Rectangular parallelepiped	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$	Axes are parallel to 2-fold one or perpendicular to m; $c < b < a$	$a : b : c$
Intermediate	One	Hexagonal	Hexagonal Trigonal*	6- or $\bar{6}$-fold axis 3- or $\bar{3}$-fold axis	Prism with 120°-angle rhombic base	$a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$	Principal axis is parallel to Z, others are in plane XY	$c : a$
		Tetragonal	Tetragonal	4- or $\bar{4}$-fold axis	Prism with square base	$a = b \neq c$, $\alpha = \beta = \gamma = 90°$		
Higher	None	Cubic	Cubic	Four 3-fold axes	Cube	$a = b = c$, $\alpha = \beta = \gamma = 90°$	Axes are parallel to three 4-fold (or $\bar{4}$- or 2-fold) axes	a

* At rhombohedral orientation: $a = b = c$, $\alpha = \beta = \gamma \neq 90°$. Unit cell is a rhombohedron. Characteristic parameters of substance are: a, α.

triclinic ("thrice inclined") system: its crystals have neither symmetry axes nor planes;

monoclinic ("once inclined") system: its crystals have only one 2-fold symmetry axis or a symmetry plane, or both the 2-fold axis and the plane;

rhombic system: its crystals have a few 2-fold axes or a few symmetry planes.

The intermediate category is also divided into three systems:

trigonal system—its crystals have one 3- or $\bar{3}$-fold principal symmetry axis;

tetragonal system—its crystals have one 4- or $\bar{4}$-fold principal symmetry axis;

hexagonal system—its crystals have one 6- or $\bar{6}$-fold principal symmetry axis.

The higher category consists of a single, *cubic*, system which is characterized by four 3-fold symmetry axes.

The categories can also be divided into six systems instead of seven.

The division into seven or six systems is generally coincident, except for the trigonal and hexagonal systems. The division into six systems determines the choice of a crystallographic system of coordinates and its three basic vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, or, in other words, its parameters a, b, c, α, β, γ (see Fig. 1.5).

The crystallographic coordinate axes are always chosen in the direction of the symmetry axes or perpendicular to symmetry planes. Should there be no corresponding symmetry elements, as in the monoclinic and triclinic systems, the coordinate axes are chosen in the direction of the edges of the crystal polyhedron or the rows of crystal lattice.

Primitive unit cells that correspond to each system are shown in the first column of Table 9.1 and in Table 4.1. Fig. 4.1 shows the choice of coordinate axes in crystals of the seven systems.

The higher category has only one system—the cubic one. It is the only system whose symmetries correspond to the common Cartesian system coordinates: $a = b = c$, $\alpha = \beta = \gamma = 90°$. The unit cell is a cube. The coordinate axes are three mutually perpendicular 4-, $\bar{4}$-, or 2-fold axes. Besides, the cubic system crystals always have four 3-fold axes (spatial diagonals of a cube), this being the most characteristic feature of cubic crystals. Whether there are six or seven systems, the cubic system is the same in both cases.

In the six-system division the intermediate category contains two systems:

the tetragonal system where the principal axis is a 4- or $\bar{4}$-fold one;

the hexagonal system where the principal axis is a 6- or $\bar{6}$-fold one, or a 3- or $\bar{3}$-fold one.

The principal axis in these systems is always the Z (X_3) one, axes X (X_1) and Y (X_2) being located in a plane perpendicular to the principal one. Intercepts along the X and Y axes are equal ($a = b$). Therefore the metric of the intermediate category crystals is characterized by the ratio c/a; this ratio varies in different substances and is the characteristic constant of a substance.

The division of categories into six or seven systems is coincident as far as the tetragonal crystals are concerned. As to the crystals

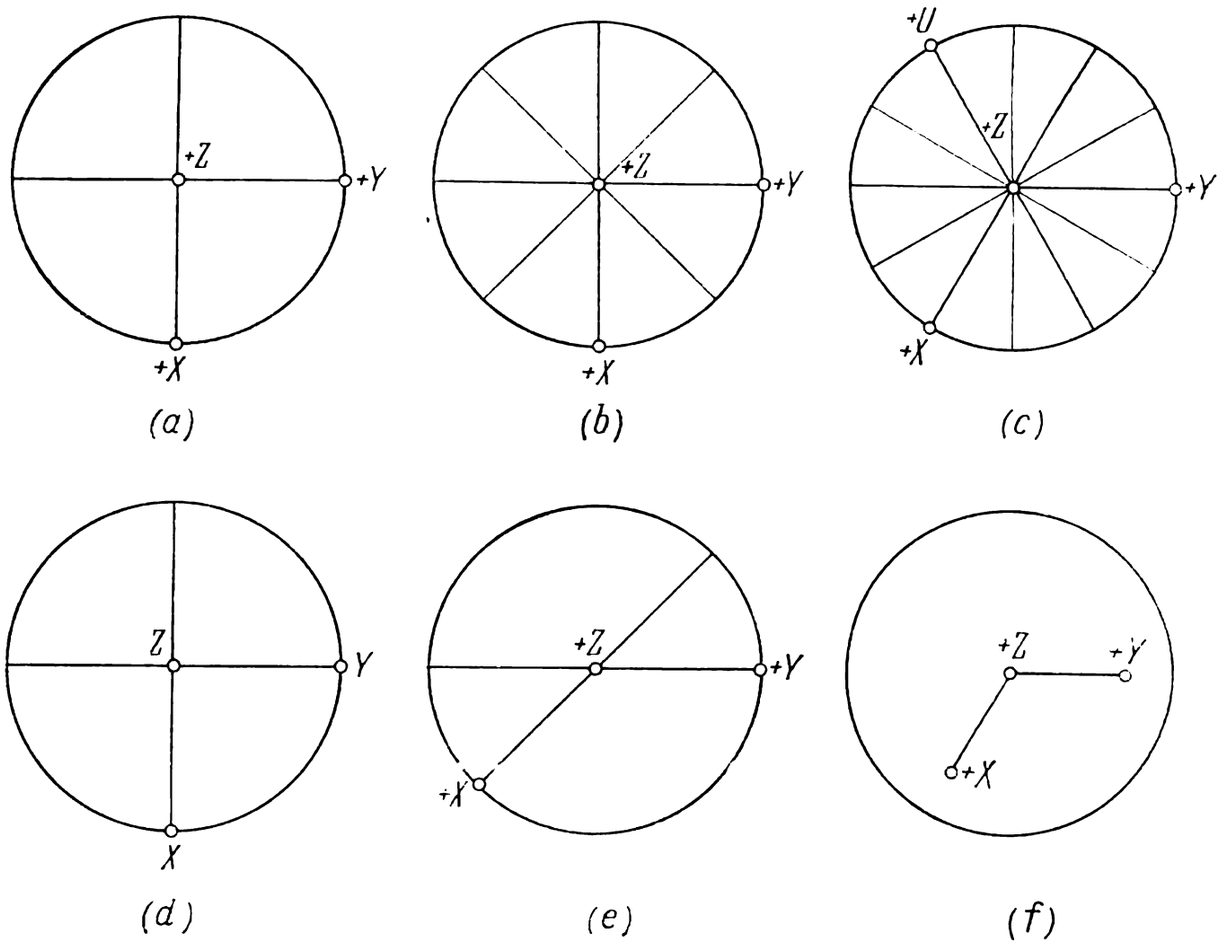


Fig. 4.1. Standard rules for crystallographic orientation (stereographic projection): cubic (a); tetragonal (b); trigonal and hexagonal (c); rhombic (d); monoclinic (e); and triclinic (f) systems

of the hexagonal and trigonal systems*, they can be described in one, so-called hexagonal system of coordinates: the only 3- or $\bar{3}$-fold axis (former case), 6- or $\bar{6}$-fold axis (latter case) is taken as axis Z. Axes X and Y, located in a plane perpendicular to the Z axis, have

* Unfortunately, the classification into six or seven systems is sometimes ambiguous. In some instances the trigonal system is regarded as a subsystem of the hexagonal system, in other cases the classification is confused, and then 7 syngonies are spoken of, including the hexagonal and trigonal syngonies. In all cases the point is not that of the differences in principle, but only that of vague terminology.

an angle of 120° between them; a fourth axis, U, is added for symmetry in the same plane and also at angle of 120°, i.e. a four-axes system of coordinates is used. The unit cell in this system consists of three primitive cells (see Tables 4.1 and 9.1).

These crystals can also be specified by a three-axes (rhombohedral) system of coordinates, its axes lying along the edges of an elementary (unit) rhombohedron, i.e. $a = b = c$, $\alpha = \beta = \gamma \neq 90°$. Angle α is the characteristic constant of the substance. The use of this system of coordinates is best justified for trigonal crystals with a rhombohedral Bravais lattice (see Sec. 9).

In the rhombic (orthorhombic) system ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$) use is made of a rectangular system of coordinates with different intercepts, $c < a < b$ being an imperative condition. The coordinate axes pass along 2-fold axes or are perpendicular to the symmetry plane.

In the monoclinic system $a \neq b \neq c$, $\alpha = \gamma = 90° \neq \beta$, axis Y is parallel to the 2-fold axis or perpendicular to m, axes X and Z lie in a plane perpendicular to Y, but their array and the angle between them are not determined by the symmetry elements, they are chosen along the rows of atoms in the structure or the edges of the external form of crystals. A different array of axes is also possible—the so-called second array of the monoclinic system, when the 2-fold axis or the perpendicular to m is arranged along the Z axis.

In the triclinic system ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$) no axes are determined by the symmetry elements, but are chosen in the direction of the edges of a crystal, the condition $c < a < b$ being imperative.

For the lower category the six and seven systems coincide.

The division of crystals into categories and systems is given in Table 4.1. It is worth mentioning that in crystallography it is highly important to adhere to the *conventions for orientation*, i.e. the location or symmetry elements along definite coordinate axes, since it provides for unambiguous indexing (see Sec. 12).

Sec. 5. Point Groups of Crystal Symmetry (Symmetry Classes)

The set of symmetry operations in an ideal crystal polyhedron, i.e. transformations resulting in the polyhedron superposing upon itself, form a *class of symmetries* or a *point group of crystal symmetry*. The number of different symmetry operations in a group is called the *order of the group*.

Let us discuss the simplest properties of such groups.

If a certain operation transforms a crystal polyhedron into itself, it will apparently be transformed into itself upon repetitions of the operation. Since the result of successive repetitions of a symmetry

operation is denoted as a power of the operation, a group contains, along with any operation, also all its possible powers. This does not mean that there can be an infinite number of powers: repetition of any crystallographic point operation will ultimately bring the crystal back to its initial position, i.e. a certain power of any such operation is equivalent to identification:

$$\bar{1}^2=1, \quad m^2=1, \quad 2^2=1, \quad 3^3=1,$$
$$4^4=1, \quad 6^6=1, \quad \bar{3}^6=1, \quad \bar{4}^4=1,$$
$$\bar{6}^6=1.$$

Groups generated by a single symmetry element, i.e. consisting of several powers of a single operation, are called *cyclic* ones. The crystallographic cyclic groups are denoted by the symbols of symmetry elements that generate them. They can be of the first order (1), of the second order ($\bar{1}$, m, 2), the third order (3), the fourth order (4, $\bar{4}$), the sixth order (6, $\bar{3}$, $\bar{6}$).

If a certain operation makes a polyhedron superpose upon itself and is, consequently, a symmetry operation, the operation that restores it to its initial position is also a symmetry operation which is the *reverse* of the initial one (the latter being the reverse of the restorative operation). A reverse operation is denoted as a minus first power of the initial one.

The product of mutually reverse operations is identification *1*; evidently, any two operations that produce identification are mutually reverse. Here are a few instances of mutually reverse operations:

$$\bar{1}\cdot\bar{1}=1, \quad m\cdot m=1, \quad 2\cdot 2=1, \quad 3^2\cdot 3=1,$$
$$4^3\cdot 4=1, \quad 6^5\cdot 6=1, \quad \bar{3}\cdot\bar{3}^5=1, \quad \bar{4}\cdot\bar{4}^3=1,$$
$$\bar{6}\cdot\bar{6}^5=1.$$

It can be seen that some operations ($\bar{1}$, m, 2) are the reverse of themselves.

If each of any two operations transforms a crystal polyhedron into itself, then successive performance of both of these operations will produce the same result: along with any two operations a group also includes their product (or both possible products, if they do not coincide).

For example, let 2_y and m_y be among symmetry operations for a certain crystal polyhedron. According to Theorem 1 (Sec. 3), $\bar{1}$ will also be a symmetry operation. These operations, together with identification, form a group, since all the possible multiplications will not result in any other operations; the symbol of this $2/m$ group is explained in the next section.

Multiplication tables of point groups $2/m$, 222, $mm2$ and of an abstract non-cyclic group of the fourth order appear as follows:

$2/m$	1	2_y	m_y	$\bar{1}$
1	1	2_y	m_y	$\bar{1}$
2_y	2_y	1	$\bar{1}$	m_y
m_y	m_y	$\bar{1}$	1	2_y
$\bar{1}$	$\bar{1}$	m_y	2_y	1

222	1	2_x	2_y	2_z
1	1	2_x	2_y	2_z
2_x	2_x	1	2_z	2_y
2_y	2_y	2_z	1	2_x
2_z	2_z	2_y	2_x	1

$mm2$	1	m_x	m_y	2_z
1	1	m_x	m_y	2_z
m_x	m_x	1	2_z	m_y
m_y	m_y	2_z	1	m_x
2_z	2_z	m_y	m_x	1

abstr.	1	a	b	c
1	1	a	b	c
a	a	1	c	b
b	b	c	1	a
c	c	b	a	1

All the multiplications in the $2/m$ group are commutative, i.e. they do not depend on the order of factors, this can be seen from the symmetry of the multiplication table of the group relative to the principal diagonal. Thus, $2/m$ is a commutative group. Obviously all the cyclic groups are commutative (but not all commutative groups are cyclic).

Those groups in which not all multiplications are commutative are called *non-commutative* ones. For instance, such is the symmetry group 32 of quartz crystals generated by a 3-fold axis and a 2-fold axis perpendicular to the former. It was shown in Sec. 3 that $3_z 2_x \neq \neq 2_x 3_z$. The multiplication table of this group is not symmetric in respect to the principal diagonal (see Sec. 3).

Group 32 is an example of groups generated by two symmetry operations. Such are also the symmetry groups of regular trihedral and tetrahedral pyramids $3m$ and $4m$. Some crystallographic groups

are generated by three operations; such as, for instance, the symmetry group of a regular tetrahedral prism $4/mmm$. Operations that generate a group are sometimes called *group generators*. Generators of all crystallographic groups are given in Table 45.2.

Sometimes a part of the operations in a group constitutes a group in itself (naturally, of a lesser order than that of the initial group); with respect to the initial group, the group of a lesser order is called a *subgroup*, while the initial one is called a *supergroup* with respect to the subgroup.

Thus, group $2/m$ has three subgroups*: $2\ \{1, 2_y\}$, $m\ \{1, m_y\}$ and $\bar{1}\ \{1, \bar{1}\}$, while group 32 has four subgroups: $3\ \{1, 3_z, 3_z^2\}$, $2\ \{1, 2_x\}$, $2\ \{1, 2_y\}$, $2\ \{1, 2_z\}$. The fact that group $\bar{1}$ is a subgroup of the $2/m$ group is denoted $\bar{1} \subset 2/m$. Group 1 consisting of a single operation 1 is a subgroup of any group; it is therefore often called a *trivial subgroup* and is omitted when subgroups are listed.

The relation of a group order to a subgroup order is called a *subgroup index*; thus, in respect of group 32 group 3 is a subgroup with index 2, while group 2 is a subgroup with index 3; in respect of group $2/m$ groups 2, m and $\bar{1}$ are subgroups with index 2.

The set of operations included in two groups simultaneously is called an *intersection* of these groups. It is not difficult to prove that the intersection of two groups is a group in itself; hence the intersection of two groups is the greatest common subgroup of these groups. When an intersection of two point groups is found, it is necessary to observe the mutual array of symmetry elements in them. Thus, if the 32 and $2/m$ groups, discussed above, are related to the same system coordinates, their intersection will form group $2\ \{1, 2_y\}$. It is denoted as $32 \cap 2/m = 2$, or if the orientation of symmetry elements is to be emphasized, $3_z 2_y \cap 2_y/m_y = 2_y$.

Point groups of crystal symmetry represent one of the possible realizations of mathematical groups. In mathematics a *group* means a set of G elements** a, b, c, . . ., satisfying the following conditions:

(1) for each two (not necessarily different) elements of the group $a \in G$ and $b \in G$ taken in a definite order, there is only one element $c \in G$ called their *product*: $(c = ab)$;

(2) the associative (combinative) law: $a\,(bc) = (ab)\,c$, is fulfilled for all elements of the group;

(3) there is a *unit element* $1 \in G$ in the group such that when multiplied from the right or from the left by any element $a \in G$, the latter does not change: $a1 = 1a = a$;

(4) for each element $a \in G$ there is a *reciprocal element* $a^{-1} \in G$ that satisfies the relation $a^{-1}a = aa^{-1} = 1$.

* Operations listed in the group are given in braces.

** An element of G, a, is denoted by $a \in G$.

A comparison of these conditions with the previously discussed properties of point groups shows that the point groups satisfy these conditions and are thus a special case of mathematical groups.

If properties of a group are only those listed in the conditions, the group is called an *abstract* one and is completely defined by its multiplication table.

Point groups have many other properties besides those listed in the conditions: they may be centrosymmetrical, acentral, holohedral and merohedral, each of the groups belonging to one or the other category, system, etc. (these latter properties are discussed in Sec. 14).

Crystallographically different point groups can be abstractly similar, i.e. they can have coincident multiplication tables (Belova, Belov, Shubnikov, 1948). Such point groups are called *isomorphous.* To all point groups different crystallographically but isomorphous between themselves, there corresponds the same abstract group; such are, for instance, the commutative groups $2/m$, 222 and $mm2$. Isomorphous groups in general are shown in Fig. 14.5.

Crystal classes (point groups) of symmetry are denoted by symbols based on the theorems on symmetry operation multiplication.

The following international notation is used: n is an n-fold axis ($n = 2, 3, 4, 6$)*, $\bar{n}$ is an n-fold inversion symmetry axis, m is a symmetry plane, nm is an n-fold symmetry axis with n symmetry planes passing along it (see Theorem 4, Sec. 3); n/m is an n-fold symmetry axis with a plane of symmetry perpendicular to it; if n is an even number, then there is also a centre of symmetry, according to Theorem 3; $n2$ is an n-fold symmetry axis with n two-fold axes perpendicular to it (see Theorem 1); $\frac{n}{m}m$ or n/mmm is an n-fold symmetry axis with planes m parallel and perpendicular to it.

In the international symbol of a symmetry class only its generating symmetry elements are written, i.e. planes or axes; a letter in the symbol meaning a perpendicular to a symmetry plane. Knowing the theorems on the combination of symmetry elements one can imagine the whole set of symmetry elements of a given class. Of the utmost importance is the order in which the symmetry element symbols are written; the single valued meaning of a digit or a letter denoting a symmetry element depends on the position which it occupies in the symbol. The conventions for writing the international symbols of point groups are given in Table 5.1. The rules for crystal orientation (Fig. 4.1) are to be strictly observed in writing the notation.

"Coordinate" and "diagonal" symmetry elements are distinguished in the international notation: the coordinate planes or axes which pass along the coordinate planes, the diagonal ones pass along the

* X or X_n is used in the international notation; here we write n, since X always denotes the first coordinate axis.

Table 5.1

The Sequence of Positions in Point Group Symbols

System	Position in a symbol		
	I	II	III
Triclinic	One symbol corresponding to any direction in a crystal		
Monoclinic	2-fold axis or perpendicular to m along axis X_2 (1st orientation) or axis X_3 (second orientation)		
Rhombic	2-fold axis or perpendicular to m along axis X_1	axis X_2	axis X_3
Hexagonal* Tetragonal	Principal symmetry axis	2-fold axes or perpendicular to m along	
		coordinate directions	diagonal directions
Cubic	Coordinate symmetry elements	3	Diagonal symmetry elements

* In rhombohedral orientation — principal axis along ⟨111⟩, 2-fold axes or perpendiculars to planes along three directions ⟨110⟩ and three directions ⟨112⟩. French quotes denote here the ensemble of symmetrically equivalent directions (see Sec. 12).

bisectrices of the angles between planes or axes. The expediency of such a distinction and the disparity of the coordinate and diagonal symmetry elements will be perceived upon a discussion of the microscopic symmetry of crystals (Sec. 9).

In the symbols of all classes of the intermediate category the first place is occupied by the principal symmetry axis located along the Z axis, the second place, by coordinate symmetry elements in the XY plane, the third place, by the diagonal symmetry elements in the same plane. The directions passing along the bisectrices of angles $\alpha = 60°$, i.e. in the cases of axes 6 and $\bar{6}$ in the hexagonal system, are sometimes traditionally called *apophemal*, the term "diagonal" being used only for the directi ns corresponding to the bisectrices of right angles, i.e. for the tetragonal system. For the 3 and $\bar{3}$-fold axes the angle $\alpha = 120°$, $\alpha/2 = 60°$, all the directions with 60° angles between them are symmetrically equivalent, therefore the third position in the symbol is vacant. For example, symbol *4mm*

means that there is one four-fold axis 4_z, two coordinate symmetry planes and two symmetry planes which pass along the principal axis 4_z and the bisectrices of the angles between the axes X and Y. This symbol can be contracted to $4mm \equiv 4m$, it being evident from Theorem 4 that if there is a plane m along the four-fold axis, then there are four such planes on the whole. Class $6mm$ is similarly written in the hexagonal system, while in the trigonal system it is enough to write $3m$, as follows from the above considerations.

In the international symbol of a point group for crystals of the higher category (cubic system) a digit 3 in the second position conventionally symbolizes four 3-fold axes, in distinction from 3 in the first position where it symbolizes one—singular—3-fold axis for the crystals of the trigonal system. The availability of four 3-fold axes passing along the bisectrices of the coordinate angles is a feature of all classes of the cubic system. 4-fold or 4-fold symmetry axes, if available, always coincide with the coordinate axes in the cubic system. 2-fold symmetry axes and planes can be coordinate or diagonal ones. If there are three 2-fold symmetry axes or planes m, these elements are coordinate, if there are six of them, they are diagonal. And if there are nine, three of them are coordinate and six are diagonal. Planes are prevalently written as coordinate and diagonal symmetry elements, while symmetry axes are included in a symbol only when there are no planes.

For example, symbol $m3$ signifies the following: four 3-fold axes along the bisectrices of the coordinate angles and three coordinate symmetry planes; according to Theorem 2, three 2-fold axes appear at the intersection of planes, while according to Theorem 3, a centre of symmetry is additionally generated at their intersection. Let us compare symbol $m3$ with symbol $3m$: 3 in the first position means the only principal 3-fold symmetry axis, i.e. a crystal belonging to the trigonal system, the letter m next to the digit means three symmetry planes passing along the axis. This example shows that the permutation of letters or digits in a symbol completely changes the latter's meaning.

In Bravais symbols the following notation is used: symmetry plane is P, centre of symmetry is C, symmetry axes are L_1, L_2, L_3, L_4, L_6, inversion symmetry axes are $L_{\bar{1}}$, $L_{\bar{2}}$, $L_{\bar{3}}$, $L_{\bar{4}}$, $L_{\bar{6}}$ or L_{i1}, L_{i2}, L_{i3}, L_{i4}, L_{i6}. In a formula of a symmetry class all symmetry elements are written one after the other: first, the axes, beginning with the higher orders, next, the planes, then, the centres. Thus, for instance, the symbol $L_6 7PC$ means that there is one axis L_6, seven symmetry planes and a centre of symmetry. According to Theorem 4, only six planes can pass along the L_6 axis, so that the seventh symmetry plane should differ in location from the other six; the presence of the centre of symmetry $C(\bar{1})$ shows, according to Theorem 3a,

that this plane ought to be perpendicular to the axis L_6 (6). Other symmetry formulas are read in the same way.

In Schoenflies notation the following symbols are used: C_n is an n-fold symmetry axis, D_n is an n-fold symmetry axis and n two-fold axes perpendicular to it. A single axis is always considered to be vertical, i.e. to be axis Z. When there are several axes, the one of the highest order is considered to be vertical. Indices v, h and d mean symmetry planes; they are respectively: v—vertical planes, h—horizontal ones, d—diagonal ones. If both types of planes are available, only the coordinate ones are included in the symbol. Letter T means the ensemble of the symmetry axes of a cubic tetrahedron, O means the set of symmetry axes of a cubic octahedron (see Fig. 6.3).

Thus C_n is a vertical polar n-fold axis, C_{nv} is a vertical polar n-fold axis with n symmetry planes passing along it, C_{nh} is one n-fold axis with a symmetry plane perpendicular to it, D_n is a vertical n-fold axis, and n 2-fold symmetry axes perpendicular to it. D_{nh} is a vertical n-fold axis, a plane of symmetry perpendicular to it and n 2-fold symmetry axis, as well as the symmetry planes generated by the intersection of these elements, for example, $D_{4h}=4/mmm$; S_n is a vertical mirror-rotation axis, an n-fold one, (sometimes the symbol C_{ni} is used, where i is the sign for an inversion symmetry axis: $S\ (S_1) = \bar{2}$, $S_2 = C_i = \bar{1}$, $S_3 = C_{3h} = \bar{6}$, $S_6 = \bar{4}$, $S_6 = C_{3i} = \bar{3}$), $S_{\bar{n}}$ is a vertical n-fold inversion axis; $V = D_2$ is a combination of three mutually perpendicular 2-fold axes, $V_h = D_{2h}$ are three mutually perpendicular 2-fold axes with planes perpendicular to each of the axes; $V_d = D_{2d}$ are three mutually perpendicular 2-fold axes and diagonal planes; T are symmetry axes of a tetrahedron, T_d are symmetry axes of a tetrahedron and diagonal planes, T_h are symmetry axes of a tetrahedron and coordinate planes; O are symmetry axes of an octahedron. O_h are symmetry axes of octahedron and coordinate planes. The presence of symmetry elements not shown in a symbol follows from summation theorems.

The system of crystallographic notation suggested by academician A. V. Shubnikov, and earlier used in some Soviet books and journals, has the same intrinsic logic as the international system, though differs slightly from it. Axes and planes are denoted, according to Shubnikov, as in the international system. Perpendicularity is denoted not by an overscribed bar, but by a colon, parallelity is denoted by a point. An oblique bar, separating symbols of two axes, means that these axes make up an oblique angle. Moreover, a bar overscribed above an axis symbol means that the axis is a mirror one, in distinction from the international symbol where a similar bar means an inversion axis.

Hence, symbol $\bar{3}$ has, according to Shubnikov, the same meaning as the international symbol $\bar{6}$, and vice versa, the international symbol $\bar{6}$ corresponds to Shubnikov's symbol $\bar{3}$. Sometimes, to avoid misunderstandings, the mirror axes in Shubnikov's notation are denoted by a wavy bar. Other distinctions of Shubnikov's notation can be perceived from Table 6.1.

Sec. 6. Derivation and Description of 32 Classes of Crystal Symmetry (32 Point Groups of Symmetry)

In order to derive 32 classes of symmetry, it is necessary to discuss all the possible combinations of crystal symmetry elements intersecting at a single point. Let us choose for this purpose some initial generating symmetry element and add to it, by turns, all other symmetry elements as generating ones. On the basis of theorems of Sec. 10, from a combination of two generating symmetry elements other generated symmetry elements are derived.

Let us begin with crystals that possess singular directions, i.e. crystals of the lower and intermediate categories. We shall choose as

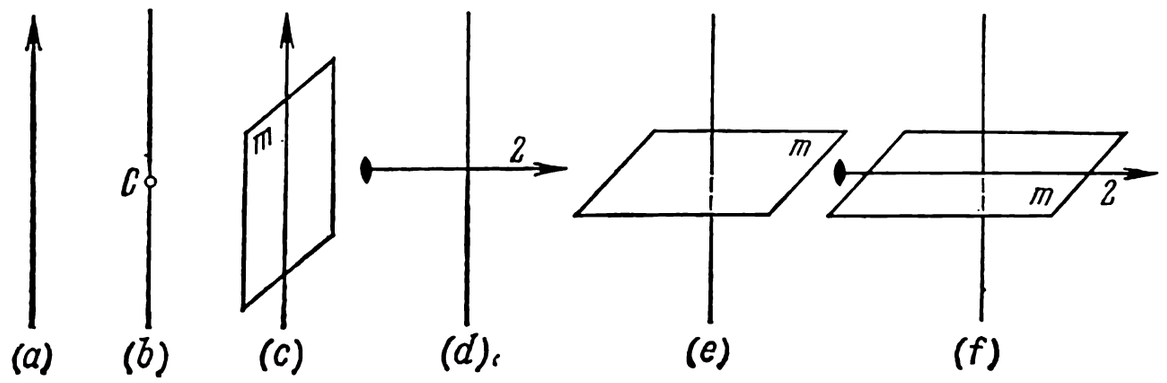


Fig. 6.1. On the derivation of symmetry classes of the lower and intermediate categories

a generating symmetry element a symmetry axis passing along a singular direction and add to it other symmetry elements as shown in Fig. 6.1. Symmetry planes can pass only through the chosen axis or perpendicular to it; otherwise the symmetry axis, having been reflected in a symmetry plane, will be repeated, i.e. will not be the only one. For the same reason 2-fold axes can only be perpendicular to the chosen axis. The centre of symmetry can be located only on the chosen axis. Therefore, in crystals of the lower and intermediate categories there can be no other combinations, except those shown in Fig. 6.1.

The *simplest*, or *primitive*, classes of symmetry are those in which there is only one symmetry element, viz. an n-fold axis along a singular direction (Fig. 6.1*a*).

Adding a centre of symmetry to each of the axes and using Theorem 3, we obtain *central classes* (Fig. 6.1*b*):

Generating axis	1-fold	2-fold	3-fold	4-fold	6-fold
Generated element	—	m	—	m	m
Symmetry class	1	$2/m$	$\bar{3}$	$4/m$	$6/m$

The addition of the centre of symmetry to a 3-fold axis has transformed it into a 3-fold inversion axis. Class $\bar{3}$ is sometimes referred

Table 6.1

32 Symmetry Classes: notation and names

Nos	International symbol		Symmetry formula	Schoenflies symbol	Shubnikov's symbol	Name, according to		
	Contracted	Full				Fedorov Institute	Schoenflies	Groth
				Triclinic system				
1	1		L_1	C_1	1	primitive	hemihedry	monohedral
2	$\bar{1}$		C	$C_i = S_2$	$\bar{2}$	central	holohedry	pinacoidal
				Monoclinic system				
3	2		L_2	C_2	2	axial	hemihedry	dihedral axial
4	m		P	$C_s = C_{1h}$	m	planal	hemimorphy	domatic
5	$2/m$		L_2PC	C_{2h}	$2:m$	planaxial	holohedry	prismatic
				Rhombic system				
6	222		$3L_2$	$D_2 = V$	$2:2$	primitive	enantiomorphous hemihedry	Rhombic-tetrahedral
7	mm	$2mm, mm2$	$L_2 2P$	C_{2v}	$2 \cdot m$	central	hemimorphy	rhombic-pyramidal

8	mmm	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	$3L_2 3PC$	$D_{2h}=V_h$	$m\cdot 2:m$	axial	holohedry	rhombic-dipyramidal
				Trigonal system				
9	3		L_3	C_3	3	primitive	rhombohedral tetartohedry	trigonal-pyramidal
10	$\bar{3}$		$L_3C=L_{3i}$	$C_{3i}=S_6$	$\bar{6}$	central	hexagonal tetartohedry	rhombohedral
11	32		$L_3 3L_2$	D_3	$3:2$	axial	enantiomorphous hemihedry	trigonal trapezohedral
12	$3m$		$L_3 3P$	C_{3v}	$3\cdot m$	planal	hemimorphous hemihedry	ditrigonal-pyramidal
13	$\bar{3}m$	$\bar{3}\frac{2}{m}$	$L_3 3L_2 3PC$	D_{3d}	$\bar{6}\cdot m$	planaxial	rhombohedral holohedry	ditrigonal-scalenohedral
				Hexagonal System				
14	6		L_6	C_6	6	primitive	hexagonal-tetartohedry	hexagonal-pyramidal
15	$\bar{6}$		L_3P	C_{3h}	$3:m$	inversion-primitive	trigonal paramorphous hemihedry	trigonal-dipyramidal
16	$6/m$		L_6PC	C_{6h}	$6:m$	central	paramorphous hemihedry	hexagonal-dipyramidal

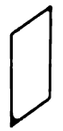
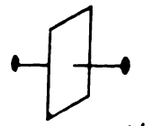
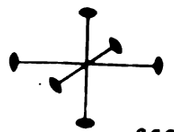
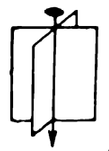
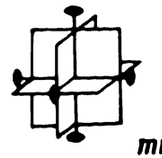
Table 6.1 (cont'd)

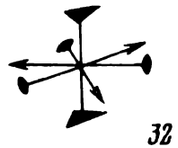
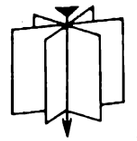
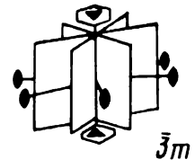
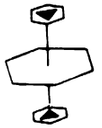
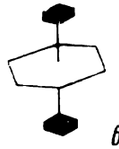
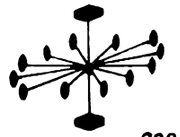
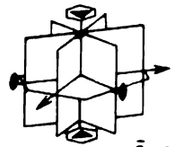
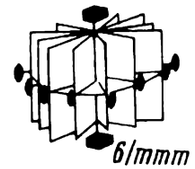
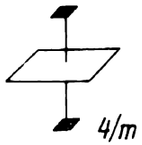
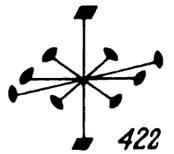
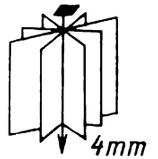
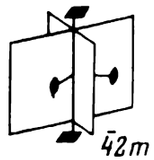
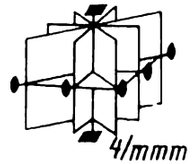
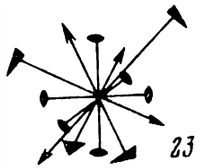
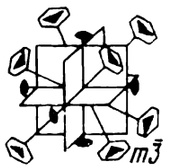
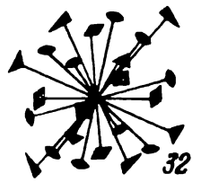
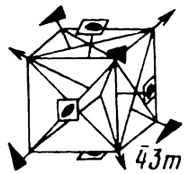
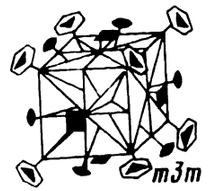
Nos	International symbol		Symmetry formula	Schoenflies symbol	Shubnikov's symbol	Name, according to		
	Contracted	Full				Fedorov Institute	Schoenflies	Groth
17	622		$L_6 6 L_2$	D_6	6 : 2	axial	enantiomorphous hemihedry	hexagonal-trapezohedral
18	$6mm$		$L_6 6P$	C_{6v}	$6 \cdot m$	planal	hemimorphous hemihedry	dihexagonal-dipyramidal
19	$\bar{6}m2$		$L_3 3 L_2 4P$	D_{3h}	$m \cdot 3 : m$	inversion-planal	trigonal holohedry	ditrigonal-dipyramidal
20	$6/mmm$	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	$L_6 6 L_2 7PC$	D_{6h}	$m \cdot 6 : m$	planaxial	holohedry	dihexagonal-dipyramidal
				Tetragonal system				
21	4		L_4	C_4	4	primitive	tetartohedry	tetragonal-dipyramidal
22	$\bar{4}$		$L_{\bar{4}}$, L_{4i}	$\bar{S}_4$	$\bar{4}$	inversion-primitive	tetartohedry of second kind	tetragonal-tetrahedral
23	$4/m$		$L_4 PC$	C_{4h}	$4 : m$	central	paramorphous hemihedry	tetragonal-dipyramidal

24	422		$L_4 4 L_2$	D_4	4 : 2	axial	enantiomorphous hemihedry	tetragonal-trapezohedral
25	$4mm$		$L_4 4P$	C_{4v}	$4 \cdot m$	planal	hemimorphous hemihedry	ditetragonal-pyramidal
26	$42m$		$L_4 2 L_2 2P$	$D_{2d} = V_d$	$4 \cdot m$	inversion-planal	hemihedry of second kind	tetragonal-scalenohedral
27	$4/mmm$	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	$L_4 4 L_2 5PC$	D_{4h}	$m \cdot 4 : m$	planaxial	holohedry	ditetragonal-dipyramidal
				Cubic system				
28	23		$3L_2 4 L_3$	T	3/2	primitive	paramorphous tetartohedry	tritetrahedral
29	$m3$	$\frac{2}{m}\bar{3}$	$3L_2 4 L_3 3PC$	T_h	$\bar{6}/2$	central	hemihedry	didodecahedral
30	432		$3L_4 4 L_3 6 L_2$	O	$\bar{3}/4$	axial	enantiomorphous hemihedry	trioctahedral
31	$\bar{4}3m$		$3L_4 4 L_3 6P$	T_d	$3/\bar{4}$	planal	hemimorphous hemihedry	hexatetrahedral
32	$m3m$	$\frac{4}{m}\bar{3}\frac{2}{m}$	$3L_4 4 L_3 6 L_2 9PC$	O_h	$\bar{6}/4$	planaxial	holohedry	hexoctahedral

Table 6.2

Assemblages of Symmetry Elements of 32 Classes

	Systems	Classes						
		Primitive	Inversion-primitive	Central	Axial	Planal	Inversion-planal	Planaxial
Lower category	Triclinic	1		$\bar{1}$				
	Monoclinic				2	 m		 2/m
	Rhombic				 222	 m2		 mmm

Intermediate category	Trigonal	3		$\bar{3}$	 32	 3m		 $\bar{3}m$
	Hexagonal	6	 $\bar{6}$	 6/m	 622	6mm	 $\bar{6}m2$	 6/mmm
	Tetragonal	4	$\bar{4}$	 4/m	 422	 4mm	 $\bar{4}2m$	 4/mmm
Higher category	Cubic	 23		 $m\bar{3}$	 32	 $\bar{4}3m$		 m3m

not to the central but to the inversion-primitive classes, see Tables 6.1 and 6.2.

Adding to the generating symmetry axis a symmetry plane passing through it, we obtain, on the basis of Theorem 4, according to scheme $m \cdot n = nm$ *planal classes* (Fig. 6.1*c*).

Generating axis	1-fold	2-fold	3-fold	4-fold	6-fold
Symmetry class	m	$mm2$	$3m$	$4mm$	$6mm$

The meaning of symbols $4mm$ and $6mm$ was explained above: in the second place are the coordinate symmetry elements, and in the third, the diagonal ones. Class $mm2$ relates to the rhombic system, in which, according to the rules for crystal orientation, the 2-fold axis (if it is the only one) should be axis 2_z and, consequently, it should take the third place in a symbol.

If we add a 2-fold axis perpendicular to the generating axis, we obtain, in accordance with Theorem 1, *axial classes* (Fig. 6.1*d*):

Generating axis	1-fold	2-fold	3-fold	4-fold	6-fold
Symmetry class	$\boxed{2}$	222	32	422	622

Class 2 is enclosed in a frame to show that this combination has already been derived. In symbols 422, 622 the 2-fold axes passing along the coordinate directions are in the second position, those passing along the diagonal directions are in the third position.

Adding to the generating axis a perpendicular symmetry plane (Fig. 6.1*e*), we obtain, according to Theorem 2a, classes that have already been listed:

Generating axis	1-fold	2-fold	3-fold	4-fold	6-fold
Symmetry class	$\boxed{m}$	$\boxed{2/m}$	$\boxed{\bar{6}}$	$\boxed{4/m}$	$\boxed{6/m}$

If we add to the generating symmetry axis a centre, a 2-fold axis and a longitudinal plane m, we obtain, according to Theorems 3 and 4, *planaxial classes* (Fig. 6.1*f*):

Generating axis	1-fold	2-fold	3-fold	4-fold	6-fold
Symmetry class	$\boxed{2/m}$	mmm	$\bar{3}m$	$4/mmm$	$6/mmm$

The listed classes exhaust the combinations of symmetry elements with a generating rotation symmetry axis.

Let us now turn to the inversion symmetry axes. We have already discussed the 1-fold, $\bar{2} \equiv m$, $\bar{3}$-fold and $\bar{6}$-fold axes. There remains only a $\bar{4}$-fold axis which generates *inversion-primitive classes*, as do the

$\bar{3}$-fold and $\bar{6}$-fold axes:

$$\bar{3},\quad \bar{4},\quad \bar{6}.$$

If to the generating inversion symmetry axis there are added symmetry planes passing through the axis, *inversion-planal classes* will be obtained:

$$\bar{4}2m \quad \text{and} \quad \bar{6}m2.$$

To begin with, let us note that any $2n$-fold inversion symmetry axis is at the same time a simple n-fold symmetry axis. Hence, according to Theorem 4, if a symmetry plane passes through the $\bar{2}n$-fold inversion axis, there should be n such planes. The resulting combination of symmetry elements obeys a new theorem*.

Theorem 6. If symmetry planes pass through an even-fold inversion axis, 2-fold symmetry axes will be located between them.

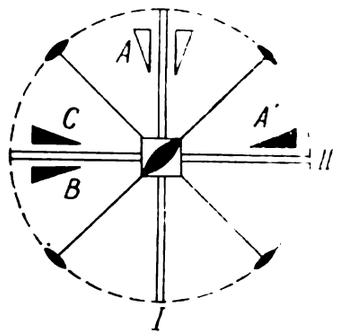


Fig. 6.2. Derivation of the $\bar{4}2m$ symmetry class

Let us illustrate this theorem for a $\bar{4}$-fold axis by Fig. 6.2. If there is given a symmetry plane *I*, there inevitably appears a symmetry plane *II*. With the aid of the $\bar{4}$-fold axis, we transfer triangle *A* through position *A'* to position *B*, and with the aid of plane *II* from *B* to *C*. But *C* could be obtained from *A* also by rotation about a 2-fold axis passing along the bisectrix of the angle between planes *I* and *II*.

Thus the $\bar{4}$-fold axis and a longitudinal symmetry plane *m* generate a second longitudinal plane *m* and two transversal 2-fold axes passing along the bisectrices of the angles between the planes. The complete combination of symmetry elements appears as $\bar{4}2m$.

Similarly, a $\bar{6}$-fold inversion axis and plane *m* passing through it generate two more longitudinal planes *m* and three transversal 2-fold axes, this resulting in $\bar{6}m2$.

No new combinations are produced by consecutive addition to the inversion symmetry axes of perpendicular planes, 2-fold axes and a centre of inversion. Thus, there were obtained 27 symmetry classes for the lower and intermediate categories (see Table 6.1).

Let us now discuss the higher category. Crystals of this category have no singular directions and can have several symmetry axes greater than 2-fold, intersecting at a single point. It was shown in Sec. 3 that only two stable combinations of symmetry axes are possible here: 4-, 3- and 2-fold and 3-, 3-, and 2-fold which correspond

* The numeration of theorems begins in Sec. 3.

to the symmetry axes of an octahedron (or cube) and to the symmetry axes of a tetrahedron (Fig. 6.3). Accordingly, we obtain two symmetry classes of the cubic system, primitive class 23 (symmetry axes of a tetrahedron) and axial class 432 (symmetry axes of an octahedron or cube).

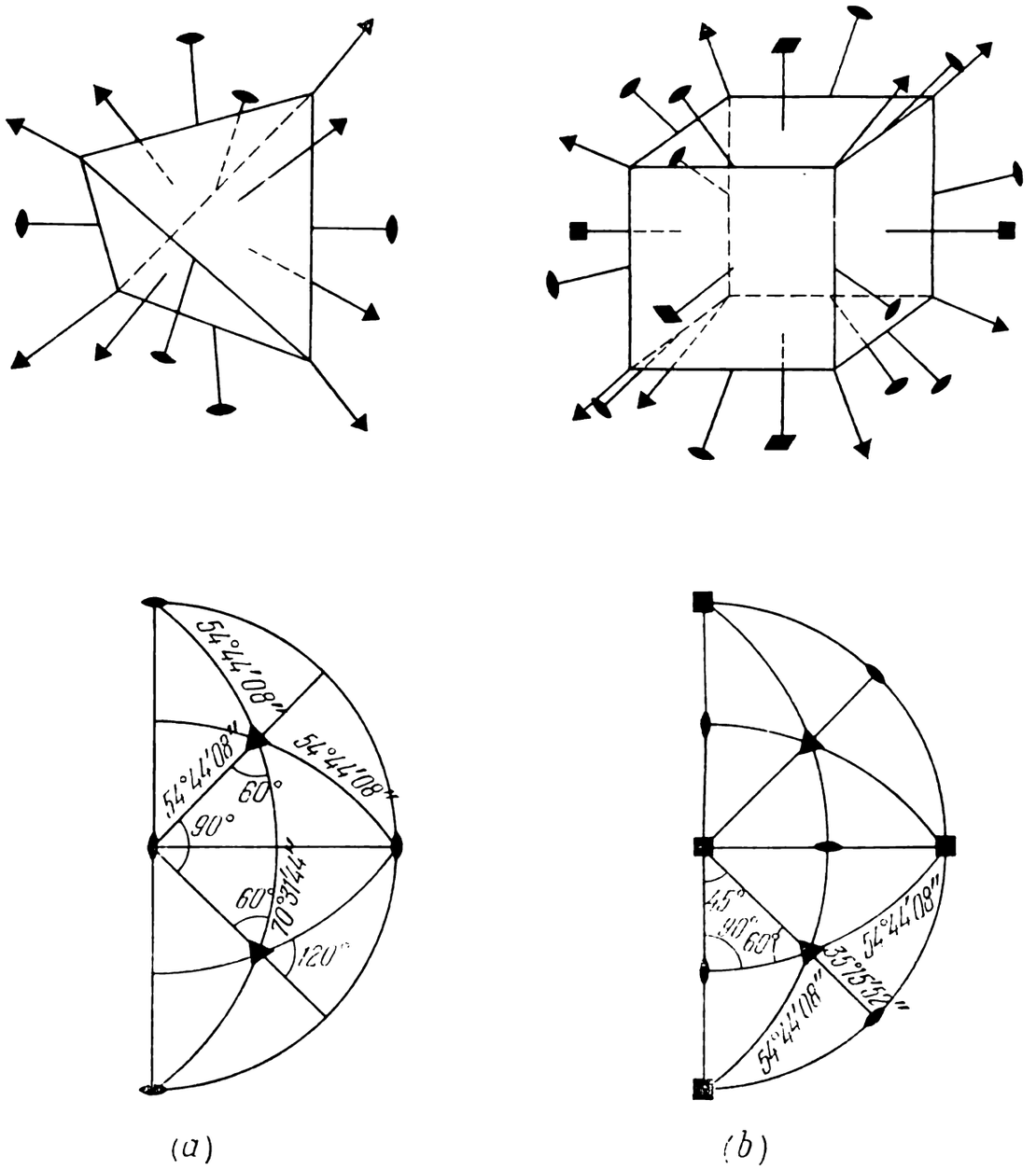


Fig. 6.3. Possible combinations of symmetry axes in crystals of the higher category: 23 (a); and 432 (b). Schemes are shown in the upper row, and stereographic projections, in the lower row.

The other classes of the cubic system can be derived just as it was done for the lower and intermediate categories, i.e. by consecutive addition of a centre of symmetry or a plane of symmetry. No more 2-fold axes can be added, since all the possible combinations of axes have been exhausted.

Only three coordinate planes or six diagonal ones can be added. No other arrays of planes are possible, because there would appear new axes at the intersections of planes. Planes perpendicular to even-fold axes will give the centre of symmetry (Theorem 2).

Let us consider all the combinations:

Generating elements		Generated elements	Results
23 23	$\bar{1}$ m through 2-fold axis	Three coordinate planes $\bar{1}$	$m3$ $m3$
23	m through 3-fold axis	Six diagonal planes 2-fold axes become 4-fold	$\bar{4}3m$
432 432 432	$\bar{1}$ m through 4-fold axis m through 3-fold axis	Three coordinate planes Six diagonal planes Centre of symmetry Six diagonal planes Three coordinate planes Centre of symmetry	 $m3m$ $m3m$ $m3m$

Thus we finally obtain five symmetry classes for the cubic system:

$$23, \quad m3, \quad 432, \quad \bar{4}3m, \quad m3m.$$

The complete list of the 32 symmetry classes and their distribution by systems is given in Table 6.1. In Tables 6.2 and 6.3 plots of symmetry elements and stereographic projections of sets of symmetry elements of each class are given.

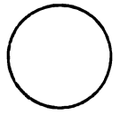
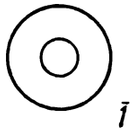
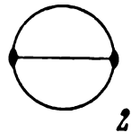
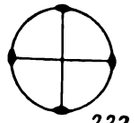
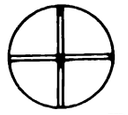
Table 6.1 gives the names of symmetry classes and their symbols: the system of the Fedorov Institute (Society) at the Leningrad Mining Institute, which has been explained in the course of derivations, and the systems of names, according to Groth and Schoenflies, which are explained below.

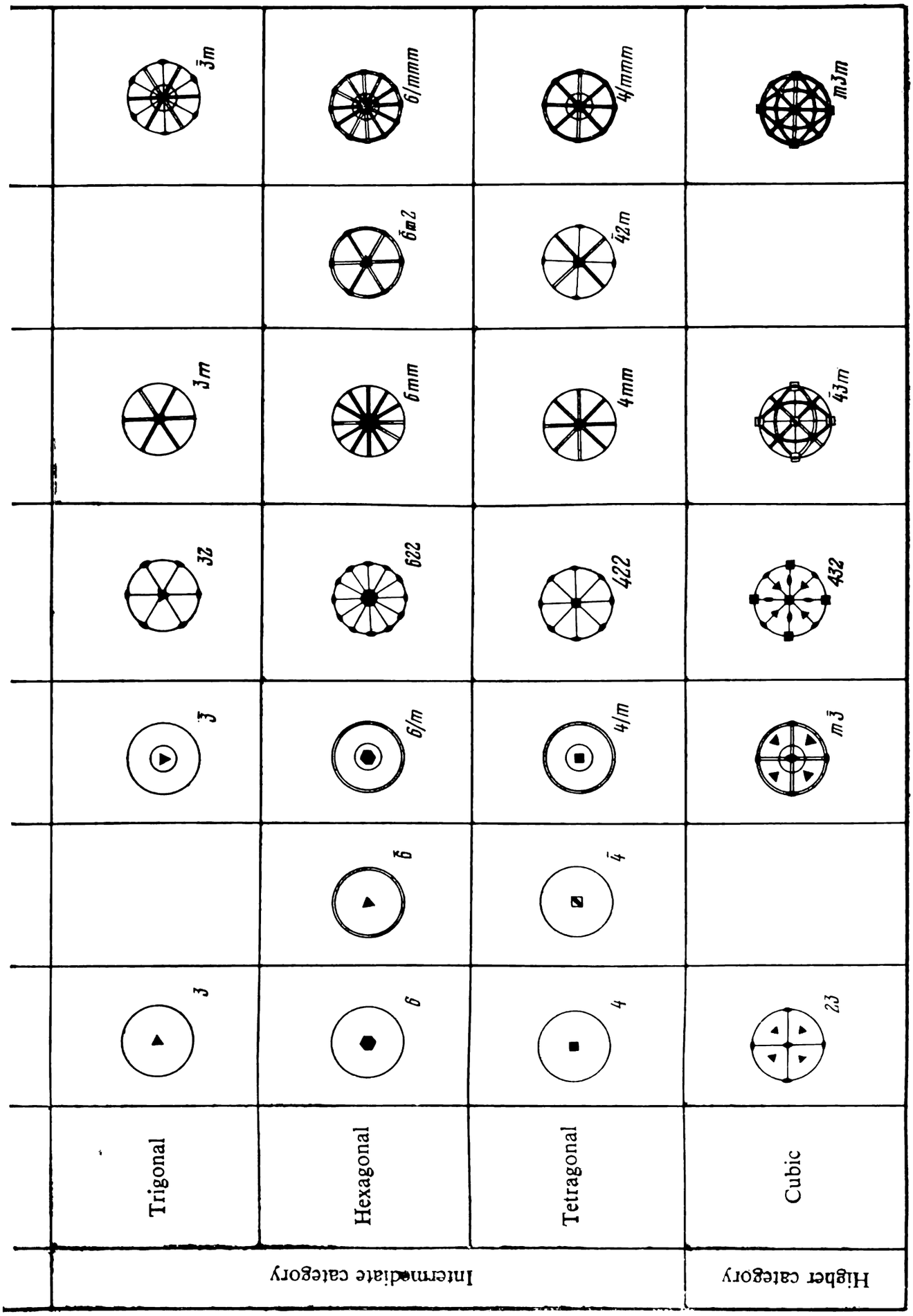
Besides divisions into systems, the 32 symmetry classes can be subdivided into larger groups depending on the following characteristic symmetry.

1. The presence or absence of a centre of symmetry. Central and planaxial classes cannot have any polar directions, consequently there can be no properties specified by a polar symmetry; the remaining 21 classes are acentral.

2. Enantiomorphism. Crystals of classes which have only rotation symmetry axes, but no inversion ones, no transverse planes and no centre of symmetry, can have right- and left-handed modifications. They can have right- and left-handed forms (see Fig. 3.6)

tereographic Projections of the Assemblages of Symmetry Elements of 32 Classes *Table 6.3*

	Systems	Classes						
		Primitive	Inversion-primitive	Central	Axial	Planal	Inversion-planal	Planaxial
Lower category	Triclinic	 1		 $\bar{1}$				
	Monoclinic				 2	m		2/m
	Rhombic				 222	 mm		mm2


Intermediate category
Higher category
Trigonal
Hexagonal
Tetragonal
Cubic
3
3̄
32
3m
3̄m
6
6̄
622
6mm
6̄m2
6/m
6/mmm
4
4̄
422
4mm
4̄2m
4/m
4/mmm
23
m3̄
432
4̄3m
m3̄m

and such properties as the rotation of the plane of polarization*. Primitive and axial classes are enantiomorphous.

3. Laue symmetry classes or subsystems. According to Friedel's law, or the law of centrosymmetry of diffraction effect, the diffraction symmetry of a crystal is higher than its point symmetry due to the symmetry of X-rays reflection. The former corresponds to the point group but plus a centre of inversion and plus the symmetry elements generated by the addition of a centre of inversion. The subsystems are shown in Table 7.1; in the lower category they coincide with the systems, in the intermediate and higher categories each system is subdivided into two subsystems: a higher and a lower one. Each subsystem includes one centrosymmetrical class and an enantiomorphous one; it can have other classes, but not necessarily. The subsystems are also called *Laue classes* and are denoted by the symbols of centrosymmetrical classes contained in them.

Sec. 7. Limit Groups of Symmetry (Curie Groups)

In Sec. 1 there was mentioned the dual approach to the study of crystals and of their physical properties. In the study of the geometry of crystal structure and the properties that depend on the defects of structure, it is necessary to regard crystals as discrete media, while in the study of certain physical properties (thermal, electrical, optical, elastic, etc.) a crystal can be regarded as a homogeneous continuous medium**. In the latter case the symmetry groups of a crystal contain only 2-, 3-, 4-, 6-fold axes, but the symmetry groups of the properties of such a medium can also include symmetry axes of an infinite order, which we shall denote by ∞. Besides, the ∞ axes can be contained in the symmetry groups of physical fields: the electric and magnetic fields, the field of mechanical stresses.

The point symmetry groups which include the infinite symmetry axes are called *the limit groups of symmetry* or *Curie groups*. There are seven such groups, and each of the 32 point groups of crystal symmetry is a subgroup of at least one limit point group, and is subordinate to the one of them which is the nearest limit supergroup with respect to the subgroup (Table 7.1). Thus, for instance, the limit group of symmetry specified by an infinite symmetry axis has crystal subgroups 6, 4, 3, 2, 1 which are subordinate to this particular limit group, although all the other limit groups are also their supergroups. A geometric figure corresponding to the ∞ point group is the rotating cone: it coincides with itself at a rotation through

* Rotation of the plane of polarization is possible not only in enantiomorphous crystals (see Sec. 81).

** See note on page 17.

Table 7.1

Crystallographic and Limit Classes
(International and Schoenflies Notation)

Subsystem		lower			higher			
Category	Class / System	primitive	inversion-primitive	central	axial	planal	inversion-planal	planaxial
lower	triclinic	1 C_1		$\bar{1}$ C_i				
	monoclinic				2 C_2	m C_{1h}		$2/m$ C_{2h}
	rhombic				222 $D_2 = V$	$mm2$ C_{2v}		mmm $D_{2h} = V_h$
intermediate	trigonal	3 C_3		$\bar{3}$ C_{3i} S_6	32 D_3	$3m$ C_{3v}		$\bar{3}m$ D_{3d}
	tetragonal	4 C_4	$\bar{4}$ S_4	$4/m$ C_{4h}	422 D_4	$4mm$ C_{4v}	$\bar{4}2m$ $D_{2d} = V_d$	$4/mmm$ D_{4h}
	hexagonal	6 C_6	$\bar{6}$ C_{3h}	$6/m$ C_{6h}	622 D_6	$6mm$ C_{6v}	$\bar{6}m2$ D_{3h}	$6/mmm$ D_{6h}
higher	cubic	23 T		$m3$ T_h	432 O	$\bar{4}3m$ T_d		$m3m$ O_h
Curie groups	textures	∞ C_∞		∞/m $C_{\infty h}$	$\infty 2$ D_∞	∞m $C_{\infty v}$		∞/mm $D_{\infty h}$
	isotropic bodies				$\infty\infty$ R			$\infty\infty/m$ R_i

any angle about the symmetry axis, but has no other symmetry elements (Fig. 7.1).

The same cone without rotation is specified by the point group $\infty\, m$, i.e. by an infinite symmetry axis and an infinite number of symmetry planes passing through it. The symmetry axis of the cone is polar. This kind of symmetry is inherent, for instance, in a homogeneous electric field: its symmetry axis coincides with the direction of the lines of electric force.

The symmetry of a homogeneous magnetic field is specified by the limit group ∞/m, i.e. by an infinite symmetry axis and a symmetry

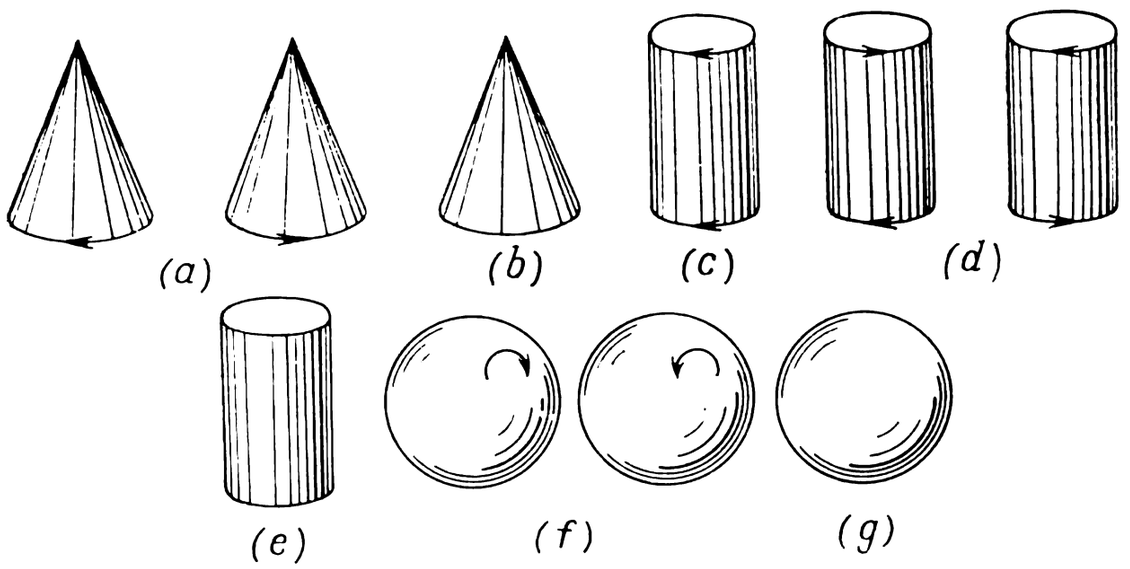


Fig. 7.1. Geometric figures symbolizing the limit point groups of symmetry: ∞, right- and left-hand (a); ∞m (*b*); ∞/m (c); $\infty 2$, right- and left-hand (d); ∞/mm (e); $\infty\infty$.right- and left-hand (f); $\infty\infty m$ (g)

plane perpendicular to it. A rotating cylinder is the characteristic figure of the ∞/m group. Groups $6/m$, $4/m$, $2/m$, m, $\bar{6}$, $\bar{4}$, $\bar{3}$, $\bar{1}$ are subordinate to the ∞/m group; crystallographic subgroups of the latter are also, besides the listed one, groups subordinate to the ∞ limit group.

Fig. 7.1 shows finite geometric solids which can specify the symmetry limit groups. A cylinder at rest, as well as an expanded or compressed one, is specified by symmetry ∞/mm, i.e. by a non-polar axis ∞, by an infinite number of longitudinal planes m, a single transversal plane m, an infinite number of transversal 2-fold axes and a centre of symmetry. A cylinder twisted about its geometric axis has $\infty 2$ symmetry, i.e. a non-polar axis ∞ and an infinite number of transversal 2-fold axes. An ordinary sphere is specified by group $\infty\infty m$, i.e. by an infinite number of axes ∞ and an infinite number of planes. This group is called an *orthogonal group*.

A peculiar body corresponding to the limit point group can be imagined as a sphere with all its radii rotating: there is an infinite

number of ∞ axes, but no symmetry planes. Group ∞∞ is called a *group of rotations.*

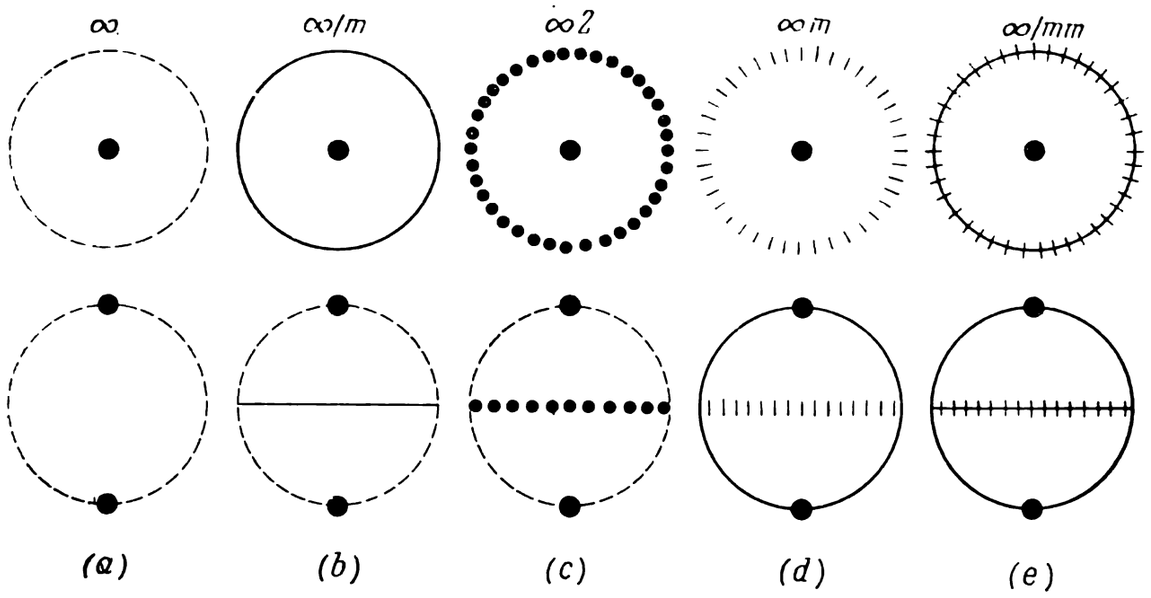


Fig. 7.2. Notation of the symmetry elements of the five Curie limit groups in stereographic projections: ∞ (a); ∞/*m* (b); ∞2 (c); ∞*m* (d); ∞/*mm* (e). In the upper row, axis ∞ is perpendicular to the plane of the paper, in the lower row, the ∞ axis is in the plane of the paper

Limit groups ∞, ∞2, ∞∞ are enantiomorphous, i.e. solids of this symmetry can be right- or left-handed. Their subordinate point groups are also enantiomorphous.

Notation of the symmetry elements of the limit groups in stereographic projections is shown in Fig. 7.2.

Sec. 8. Symmetry of Crystal Structure

In crystal structure infinite symmetric transformations are added to the finite symmetry transformations included in a symmetry point group.

The basic infinite symmetric transformation is the *translation*, i.e. an infinitely repeating transition along a single straight line to one and the same distance which is called a *period of translation**. The product of translation by an operation of reflection in a symmetry plane generates a complicated infinite symmetry operation—transformation by glide reflection. A *glide reflection plane* is a combination of a symmetry plane and a displacement parallel to the plane to a distance of half the period of translation along the plane. The action of the glide reflection plane can be shown by the example

* The term "translation" is used to denote symmetric transformation a well as a symmetry element, and, sometimes a period of translation.

of rock salt structure (Fig. 8.1 compare with Fig. 1.1). A plane net of such a structure is shown: the Na and Cl ions alternating in a checkered manner. For an ion to coincide with another like ion nearest to it, the reflection in a symmetry plane a or b should coincide with a translation by $a/2$ or $b/2$ respectively along the plane. Under such a reflection accompanied by translation, the infinitely extended plane pattern will superpose upon itself: $t_{a/2} \cdot m_a = a$ and $t_{b/2} \cdot m_b = b$.

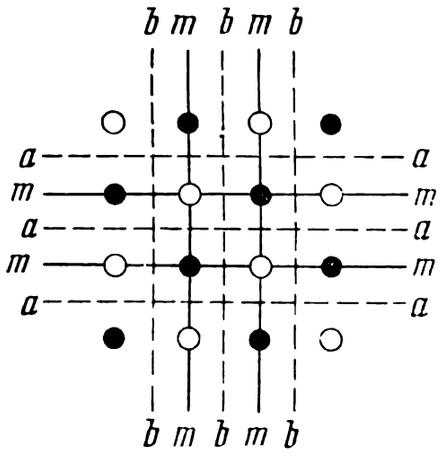


Fig. 8.1. Glide reflection planes a, b and mirror symmetry planes m in the plane net of NaCl (the structure is regarded to be infinite).

Here, the ordinary symmetry planes m alternating with the glide reflection planes pass through the centres of ions. The number of either kind of planes is infinite. The glide reflection planes are denoted by a, b, c, if the glide is in the direction of a, b, c (X, Y, Z) axes respectively, and its magnitude is $a/2$, $b/2$, or $c/2$.

The glide may also be directed along the diagonal of a parallelogram formed by elementary translations a, b, c in the glide plane. If the translation is done to half the length of the parallelogram diagonal, the plane is denoted by symbol n, if to the quarter length

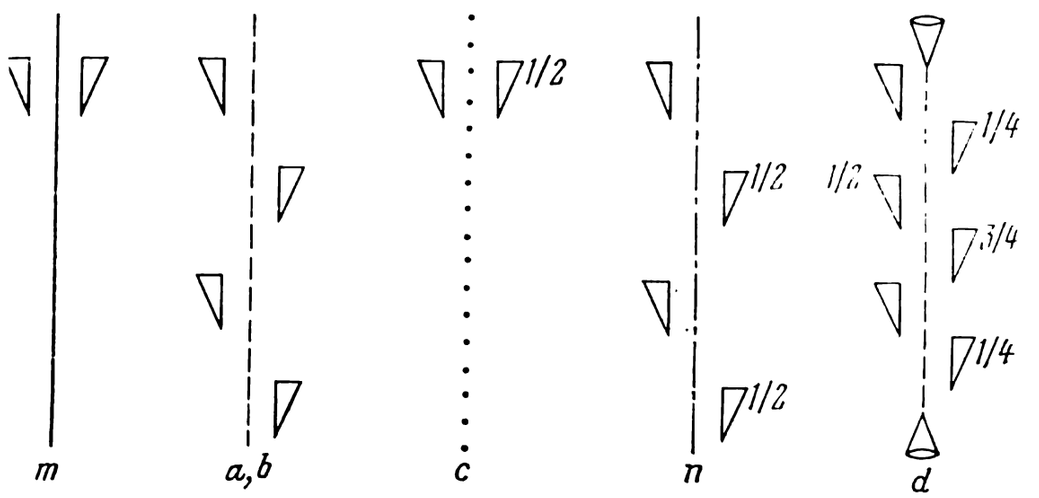


Fig. 8.2. Mirror reflection planes m and glide reflection planes a, b, c, n, d

of the diagonal, by symbol d; planes d are called "diamond" ones, since they are characteristic of the diamond structure. The glide reflection planes are shown by dashed and dotted lines (Fig. 8.2). When reflected in the glide reflection plane c, a figure moves by half the period of translation of the axis c perpendicular to the plane of the paper. To show the position of the figure at the height of $c/2$ above the plane of the paper, the number "1/2" is written at its side.

Similarly, 1/4 or 3/4 show that the figure is located at the height of $c/4$ or $3c/4$ above the plane of the paper. Symmetric transformation by the glide reflection plane can be specified by showing the corresponding change of the coordinates x, y, z of an arbitrary point.

The product of translation by rotation about the symmetry axis generates a screw rotation. The symmetry axis together with a translation along it, acting *simultaneously*, is called a *screw axis of symmetry*. Upon a complete revolution the initial point should coincide with another point, quite identical with it, i.e. removed from it by one or several periods of translation. Screw axes of symmetry can be characterized, for example, by the arrangement of maple leaves on their branch, of grains in an ear of corn, of scales on a pine cone. A screw with a round nut has a screw symmetry axis of an infinite order, but if the nut is hexagonal, the screw axis is six-fold. The screw symmetry axes in crystal space can only be 2-fold, 3-fold, 4-fold, 6-fold (Fig. 8.3). A screw axis is denoted by a digit with a digit subscript: the digit shows, as usually, the order of the axis,

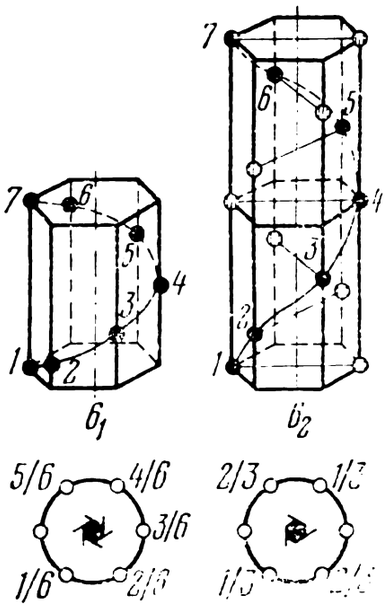


Fig. 8.3. Screw symmetry axes 6_1 and 6_2

Table 8.1

Notation of Symmetry Elements of Crystal Structures

Axes			Planes		
vertical	horizontal	inclined	vertical	horizontal	inclined
2, 6, 2_1, 6_1, 3, 6_2, 3_1, 6_3, 3_2, 6_4, 4, 6_5, 4_1, $\bar{1}$, 4_2, $\bar{4}$, 4_3, $\bar{6}$	2, 2_1, 4, 4_1, 4_2, 4_3, $\bar{4}$	2, 2_1, 3, 3_1, 3_2	m, a,b, c, n, a	m, a, b, c, n, a	m, a,b, n,c

the quotient of the division of subscript by the axis order gives the magnitude of the translation along the axis in fractions of the elementary translation along it.

There are right- and left-hand screw axes. The notation of all the screw axes and glide reflection planes used in the international system is given in Table 8.1.

In Shubnikov's notation the screw axes are denoted by a point over the name of the axis; the right-handed screw axis is denoted by the plus sign, the left-handed one by minus sign.

Shubnikov's notation is given below (the second line) as compared with the international ones (the first line) of the right-handed screw axes:

2_1	3_1	3_2	4_1	4_3	6_1	6_5	6_3	6_4	6_2	
$\pm\dot{2}$	$+\dot{3}$	$-\dot{3}$	$+\dot{4}$	$-\dot{4}$	$+\dot{6}$	$-\dot{6}$	$\dot{2}.3$	$+\dot{3}.2$	$-\dot{3}.2$	$\pm\dot{4}.2$

Sec. 9. Combinations of the Symmetry Elements of Structures. Bravais Lattices. Generation of New Symmetry Elements

The principal symmetric transformation of crystal structures is an infinite repetition; not a single point remains in its place, they are all infinitely repeated by means of translations. Crystal structure consists of particles or groups of particles connected with one another by different transformations of symmetry. The combination of translations with each of the symmetry elements generates new symmetry elements, infinitely repeating themselves in space.

Each structure has its particular set of elementary translations, or a ***translation group***, which defines its *space lattice*.

Depending on the ratio between magnitudes, and mutual orientation of three basic translations, a, b, c, there are produced lattices differing from each other by their symmetries. Symmetry restricts the number of possible lattices. All crystal structures are described by 14 translation groups that correspond to 14 Bravais lattices. An infinite system of points formed by translational repetition of one point is called the *Bravais lattice*.

The 14 Bravais lattices differ from each other by the shape of their unit cells and kind of symmetry and are subdivided into 6 systems. The subdivision into systems was introduced as early as the beginning of the 19th century and was based simply on the study of the external forms of minerals. In 1848 Bravais arrived at the same division into systems in solving the problem of symmetric arrangement of spherical particles (material points) in space.

The symmetry of crystal space restricts the number of possible crystal lattices. A lattice must be invariant in respect of all symmetric transformations possible for a given crystal space.

We shall consider the principle of the derivation of Bravais lattices citing two-dimensional lattices as an example. A plane grid is defined by a pair of base vectors, $\boldsymbol{a}_1$, $\boldsymbol{a}_2$; the parameters of a cell are a, b, γ. The plane net should be compatible with rotations about 1-, 2-, 3-, 4-, 6-fold axes, perpendicular to the plane of the net, and with reflections in symmetry planes also perpendicular to the same plane; no symmetric transformation removing the lattice from its plane is compatible with the plane net.

Only 10 point groups (Fig. 9.1): 1, 2, 3, 4, 6, m, $mm2$, $3m$, $4mm$, $6mm$ of the 32 point groups of symmetry are suited for plane systems. Only these combinations of symmetry elements leave the point in the given plane. In all two-dimensional point groups the principal symmetry axis is perpendicular to the plane discussed, and the symmetry planes pass through this axis. Formally it can be accepted for group m that plane m passes through the 1-fold axis perpendicular to the plane.

What values of the translations (a and b) and of angle γ between them are possible in plane nets? In the general case $a \neq b$, $\gamma \neq 90°$, and we obtain an oblique-angled net with unequal-sided cells. Rotations about 1- and 2-fold axes are compatible with it. The presence of a 4-fold axis calls for a square lattice, i.e. for $a = b$ and $\gamma = 90°$. The presence of 3- and 6-fold axes calls for a hexagonal lattice, i.e. for $a = b$ and $\gamma = 120°$.

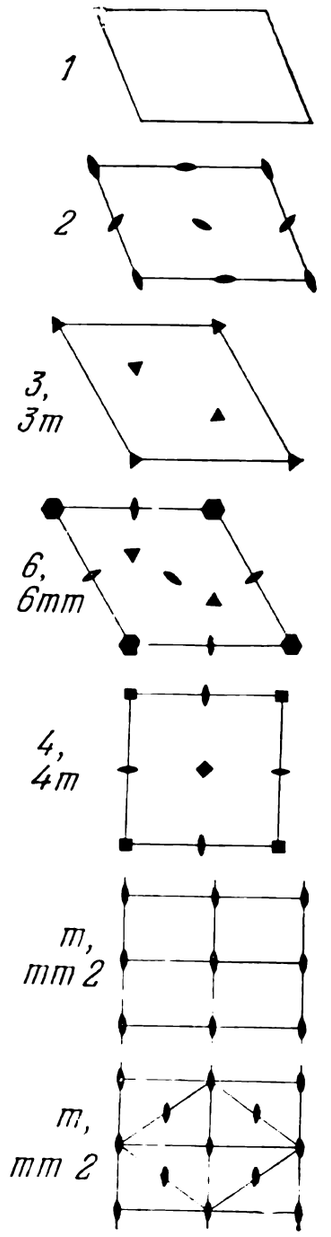


Fig. 9.1. Combinations of symmetry elements corresponding to the point groups of symmetry of infinite plane systems

To know what yields the presence of plane m perpendicular to the plane net, we shall express the base vectors $\boldsymbol{a}$, $\boldsymbol{b}$ in terms of unit vectors $\boldsymbol{i}$, $\boldsymbol{j}$ of the coordinate system

$$\begin{aligned} \boldsymbol{a} &= a_x\boldsymbol{i} + a_y\boldsymbol{j}, \\ \boldsymbol{b} &= b_x\boldsymbol{i} + b_y\boldsymbol{j}. \end{aligned} \tag{9.1}$$

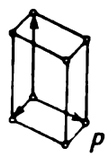
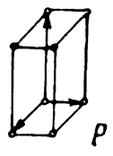
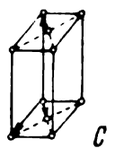
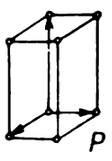
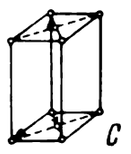
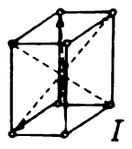
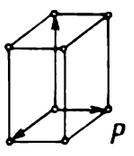
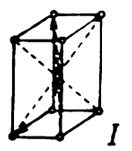
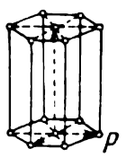
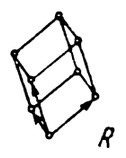
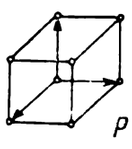
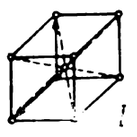
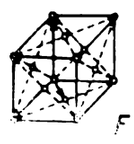
Assuming that the symmetry plane m passes through axis X, we obtain with a miror reflection in the plane

$$\begin{aligned} \boldsymbol{a}' &= a_x\boldsymbol{i} - a_y\boldsymbol{j}, \\ \boldsymbol{b}' &= b_x\boldsymbol{i} - b_y\boldsymbol{j}. \end{aligned} \tag{9.2}$$

There are only two possibilities for translations $\boldsymbol{a}'$ and $\boldsymbol{b}'$ to be also lattice translations: the first one is $\boldsymbol{a} = a\boldsymbol{i}$, $\boldsymbol{b} = b\boldsymbol{j}$, this producing a

Table 9.1

14 Bravais Space Lattices

System	Lattice				
	primitive	base--centred	body--centred	face--centred	rhombohedral
Triclinic					
Monoclinic					
Rhombic					
Tetragonal					
Hexagonal					
Cubic					

rectangular lattice: $a = b$, $\gamma = 90°$, and the second one $\boldsymbol{b}' = \boldsymbol{a} - \boldsymbol{b}$, i.e. $b'_x = a_x - b_x$, $b'_y = a_y - b_y$. This solution is obtained from (9.1) and (9.2) at $a_y = 0$, $a_x = 2b$, i.e. at $\boldsymbol{a} = a\boldsymbol{i}$, $\boldsymbol{b} = \frac{1}{2}a_x\boldsymbol{i} + b_y\boldsymbol{j}$.

In the latter case a *centred rectangular cell* is constructed on the $\boldsymbol{a}$, $\boldsymbol{b}$ translations, i.e. a cell $a \neq b$, $\gamma = 90°$, that has still another point in its centre. This lattice can also be specified with the aid of a rhombic

net, its cell being primitive, non-centred. However, a centred cell is more convenient for our purpose,because it permits using a rectangular system of coordinates.

Thus we obtain 5 Bravais plane nets: parallelograms, rectangles, rhombs, triangles and squares.

14 Bravais space lattices (Tables 9.1, 9.2) are derived in the same

Table 9.2

Notation of Cell Types and Translation Groups for 14 Bravais Space Lattices

System	Lattice				
	primitive	base-centred	body-centred	face-centred	rhombo-hedral
Triclinic	P, Γ_{tr}				
Monoclinic	P, Γ_m	C, Γ_m^b			
Rhombic	P, Γ_0	C, Γ_m^b	I, Γ_0^v	F, Γ_0^f	
Tetragonal	P, Γ_q		I, Γ_q^v		
Hexagonal	P, Γ_h				
Cubic	P, Γ_c		I, Γ_c^v	F, Γ_c^f	R, Γ_{rh}

way. Unit cells in Bravais lattices are chosen so that (1) their symmetry would correspond to the symmetry of the whole lattice*, (2) the number of right angles and equal sides would be the greatest possible, and (3) the volume of a cell would be the smallest possible.

The Bravais lattices play a tremendous role in crystallography. Any crystal structure can be represented with the aid of one of the 14 Bravais lattices that are subdivided into the following types: P—primitive, J—body-centred, F—face-centred, A, B, C—base-centred (side-centred), R—rhombohedral.

The primitive Bravais cells are the basic cells distinguishing the crystallographic systems. In the trigonal system the primitive unit cell can be, along with a prism, a rhombohedron (R)—a body in which $a = b = c$, $\alpha = \beta = \gamma \neq 90°$. In the hexagonal system the primitive unit cell is conventionally a prism with an edge parallel to a 6-fold axis and a rhombic base, $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$.

The unit cell of a hexagonal structure is a hexahedral prism composed of three unit cells; it reflects the symmetry of both the trigonal and hexagonal crystals. It is sometimes more convenient to use

* More exactly, the symmetry of a unit cell should coincide with the symmetry of the holohedral class of the system which the crystal belongs to.

for the hexagonal system a so-called *orthohexagonal cell* which is also non-primitive, for which $a \neq c$, and $b = a\sqrt{3}$.

In primitive cells the lattice points are located only at the cell vertices, in the multiple primitive cells there are more points: in the body-centred I-cell there is another point in its centre, in the face-centred F-cell there is a point in the centre of each face, in the base-centred C-cell (A or B cells) there is a point at the centre of each pair of parallel faces. The point at a cell vertex belongs simultaneously to eight adjacent cells, a point in the centre of a face, to two adjacent cells simultaneously. Thus, per volume of a cell there are: P-cell—1 point, I-cell—2 points, F-cell—4 points, C-cell—2 points.

A hexagonal primitive cell can also be described with the aid of a rhombohedral cell R, but the rhombohedron should in this case be non-primitive, it must contain two additional points [[1/3 2/3 1/3]], [[2/3 1/3 2/3]].

A rhombohedral lattice can also be regarded as a centred hexagonal one: a primitive hexagonal cell has two additional points [[00 1/3]] and [[00 2/3]].

All the four types of cells—P, I, F, C are present only in the rhombic system, other systems do not contain all the cell types (see Table 9.1). For example, the cubic system has no base-centred Bravais cell, because it would not agree with the symmetry of the cubic lattice: if one pair of faces is centred, then, due to the cube symmetry, two other pairs certainly have centres, i.e. a C-cell would become an F-cell. The tetragonal system has no C-cell; it would be compatible with the lattice symmetry but would not satisfy the requirements for the choice of a Bravais cell; a primitive cell can very well be taken instead, its volume being half that of the C-cell.

The same arguments can prove the sufficiency of the choice of all cells for all systems given in Table 9.1. The 14 Bravais lattices exhaust all the possible translation lattices specifying any of all the crystal structures.

In crystal structure the Bravais lattices can be inserted one into the other, while at the points of various lattices there can be both like and different atoms, both spherically symmetric and those having real crystallographic symmetry. All types of structures are described by 230 space groups of symmetry which are formed by the combinations of the symmetry elements of infinite structures.

The multiplication of the symmetry elements of structures obeys the same theorems 1-6 that describe the symmetry of polyhedrons. Moreover, new combinations result from the addition of infinite repetitions. Here are some of them*. We give illustrative examples

* The numeration of theorems continues that of Secs. 3, 6.

rather than rigorous proofs as we did for the multiplication of the symmetry elements of polyhedrons*.

Theorem 7. A consecutive reflection in two parallel symmetry planes is equivalent to translation by parameter $t = 2a$, where a is the interplanar distance.

In Fig. 9.2, *I* and *II*, there are two parallel symmetry planes. Reflection in plane *I* gives rise to the transformation $A \rightarrow B$, reflection in plane *II* gives $B \rightarrow C$, and it is evident from the plot at once that the distance between the corresponding points of triangles *A* and *C* equals $2a$.

The two consecutive reflections $A \rightarrow C$ and $B \rightarrow C$ can be replaced by translation $A \rightarrow C = 2t$:

$$m_{II} \cdot m_I = t. \tag{9.3}$$

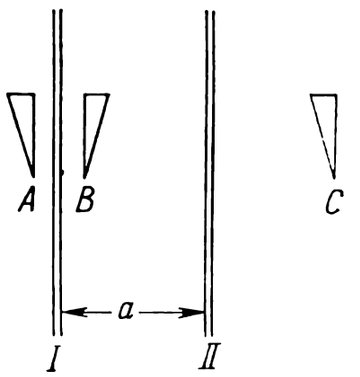


Fig. 9.2. Two parallel planes of a mirror reflection are equivalent to translation

Theorem 7a. Any translation t can be replaced by a reflection in two parallel planes removed from each other by distance $t/2$.

The theorem is the reverse of Theorem 7, is similarly proved and follows from Fig. 9.2.

Theorem 8. A symmetry plane and translation t perpendicular to it generate new, "inserted", symmetry planes parallel to the generating one, similar to the latter in type and removed from it by distance $t/2$.

In Fig. 9.3*a* translation t is perpendicular to the plane of symmetry *I*. Reflection in plane *I* produces transformation $A \rightarrow B$, translation t gives transformation $A \rightarrow C$, $B \rightarrow D$. It can be seen that *B* and *C* as well as *A* and *D* are also interconnected by a reflection in the generated (inserted) symmetry plane *II*:

$$m_I \cdot t_\perp = m_{II}. \tag{9.4}$$

Theorem 8 holds independently of the type of the generating plane: a glide reflection plane and translation t perpendicular to it generate another glide reflection plane of the same magnitude and direction of glide, the new plane is removed from the generating plane by distance $t/2$ in the direction of translation.

Fig. 9.3*b* illustrates this for an *a*-type plane (displacement along axis *X*), while Fig. 9.3*c* for a *c*-type plane (displacement along axis *Z* perpendicular to the plane of the paper). In both cases translation t is perpendicular to the generating plane *I*.

Transformation in the glide reflection plane yields $A \rightarrow B$ (Fig. 9.3*c*); in case of plane *c* the *B* and *B'* figures are raised by $c/2$

* The best and fullest deduction was given by Acad. N. V. Belov (see Belov, 1951).

above the plane of the paper, this being denoted by "1/2". Translation t produces transformations $A \to A'$ and $B \to B'$. It is apparent that at a distance $t/2$ a generated glide reflection plane II of the same type as the generating plane I passes between B and A.

Theorem 9. A symmetry plane and translation t, making up angle α with the plane, generate a glide reflection plane parallel to the

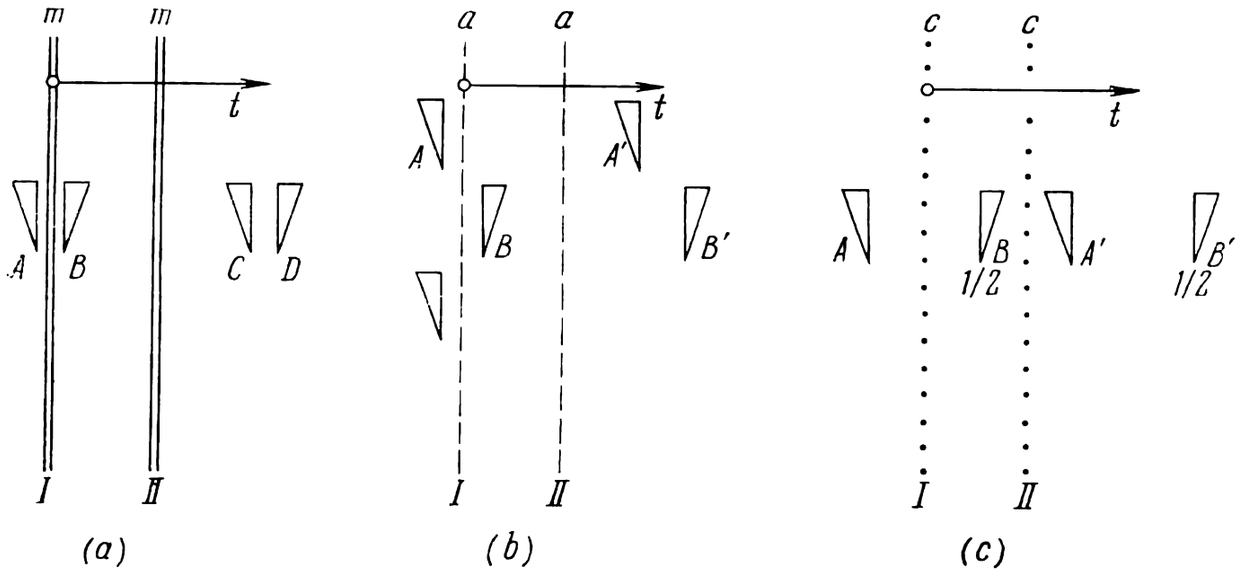


Fig. 9.3. A symmetry plane and a translation perpendicular to it generate an identically denoted inserted plane: a mirror plane (a); a glide reflection plane with displacement in the plane of the paper (b); a glide reflection plane with displacement perpendicular to the plane of the paper (c)

generating plane and removed from it in the direction of translation by $(t/2)\sin\alpha$: the magnitude of glide along the generated plane is $t\cos\alpha$.

To prove the theorem, let us decompose translation t into components $t_\perp = t\sin\alpha$ and $t_\parallel = t\cos\alpha$:

$$\mathbf{t}_\perp + \mathbf{t}_\parallel = \mathbf{t}_\alpha. \tag{9.5}$$

The combination of the generating plane with $t_\perp = t\sin\alpha$ generates, according to the preceding theorem, a similar plane parallel to the generating one and distant by $(t/2)\sin\alpha$ from it; translation $t_\parallel$ transforms this plane into a glide reflection plane with $t_\parallel = t\cos\alpha$ (Fig. 9.4).

The theorem will obviously hold for any type of generating planes. It follows from Theorem 9 that if in a point group of crystal symmetry there are symmetry planes, then there will inevitably appear in the structure of the crystal generated symmetry planes, ordinary or of glide reflection, between the generating symmetry planes. The types of generated planes depend both on the types of the generating ones and on the set of translations of the Bravais unit cell, i.e. on the type of the Bravais lattice.

Theorem 10. A symmetry axis with a rotation angle α and translation t perpendicular to the axis generate a similar symmetry axis parallel to the first one, removed from it by distance $(t/2)\sin(\alpha/2)$ and located on a perpendicular to translation t in its middle.

Let A_α (Fig. 9.5) be the point of emergence of a simple symmetry axis, with the angle of rotation α, and t, a translation perpendicular to it. According to Theorem 2a (Sec. 3), we replace the A_α axis by two intersecting symmetry planes, plotting one of the planes, $m_\perp$ (I), perpendicularly to the translation t and the second one, $m_\parallel$ (II) at an angle $\alpha/2$ to the first one. According to Theorem 7a, we replace

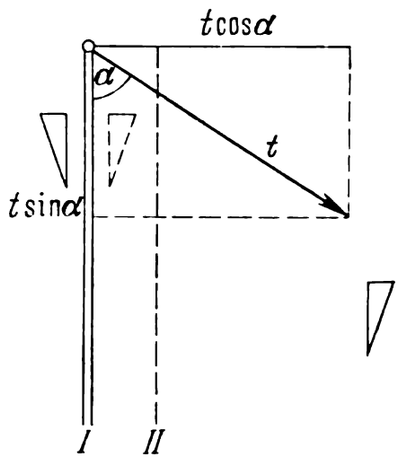


Fig. 9.4. Plane m and a translation making up angle α with it generate a glide reflection plane

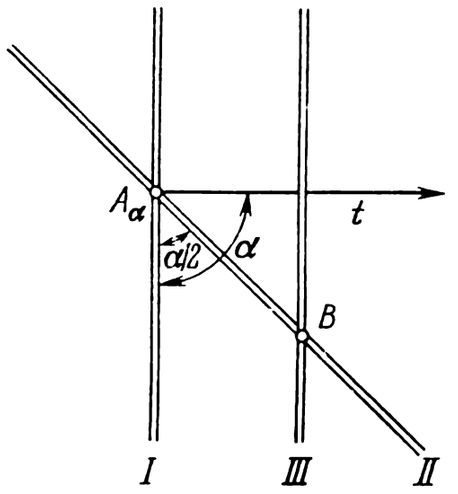


Fig. 9.5. A symmetry axis and a translation perpendicular to it generate a parallel symmetry axis

translation t by two parallel symmetry planes m_I and m_{III} (III); the plane m_{III} will cut translation t in two. Two consecutive reflections in plane m_I add up to a unit transformation

$$A_\alpha \cdot t_\perp = m_I \cdot m_{II} \cdot m_I \cdot m_{III} = 1 \cdot m_{II} \cdot m_{III}. \tag{9.6}$$

According to theorem 2 (see Sec. 3), two symmetry planes intersecting at an angle $\alpha/2$ are identical with a symmetry axis, having the angle of rotation α and passing along the line of their intersection:

$$m_{II} \cdot m_{III} = A'_{\alpha/2}, \tag{9.7}$$

i.e. they generate a symmetry axis A_α.

It can be seen from the plot that

$$AB = \frac{t/2}{\sin(\alpha/2)} = \frac{t}{2\sin(\alpha/2)}.$$

The theorem is proved.

Theorem 11. A screw symmetry axis with the angle of rotation α and displacement t_1, and translation t perpendicular to the given

axis generate a screw axis having the same angle and the same displacement. It is parallel to the given one, spaced from it by $(t/2)\sin(\alpha/2)$, and located in the middle of a perpendicular to translation t.

The proof is the same as the preceding one, the only difference being in that the screw symmetry axis $A_{\alpha t_1}$ is represented as the product of two elements, namely a simple rotation symmetry axis A_α and translation t_1 along the axis:

$$A_\alpha \cdot t_1 \cdot t_\perp = m_\perp \cdot m_{||} \cdot t_1 \cdot m_I \cdot m_{III} = 1 \cdot t_1 \cdot m_{II} \cdot m_{III} = \\ = B'_\alpha \cdot t_1 = B_{\alpha \cdot t_1}, \quad (9.8)$$

i.e. we obtain a screw axis, having the same angle of rotation α and the same displacement t_1, located at point B (Fig. 9.5).

Theorem 12. A symmetry axis with the angle of rotation α and translation t making up an angle β with the axis generate a screw symmetry axis.

To prove this, we decompose translation t into components $t_\perp = t\cos\beta$ and $t_{||} = t\sin\beta$:

$$A_\alpha \cdot t = A_\alpha \cdot t_\perp \cdot t_{||}. \quad (9.9)$$

According to (9.6)-(9.8) we obtain a screw symmetry axis with an angle of rotation α and a value of $t\sin\beta$, removed by $t/2\,[\sin(\alpha/2)]$ apart from A.

Theorem 13. A screw symmetry axis with a rotation angle α and transfer t_1, and translation t, making up an angle β with the axis, generate a screw symmetry axis having the same angle of rotation.

The proof is the same as the preceding one the difference being in that we immediately represent the screw rotation $A_{\alpha_1 t_1}$ as the product of a simple rotation and translation t_1:

$$A_{\alpha_1 t_1} = A_\alpha \cdot t_1 \cdot t_\perp \cdot t_{||} = A'_\alpha \cdot t_1 \cdot t_{||} = A'_{\alpha, T}, \quad (9.10)$$

where translation $T = t_1 \cdot t_{||}$.

It follows from Theorems 12 and 13 that if a symmetry axis passes through a vertex of a unit cell, then the combination of this axis with the Bravais group translations generates symmetry axes, both simple and screw ones, on the cell edges, in its centre and in the positions defined by the theorems.

Since the symmetry axis α includes rotations that are its multiples, the resulting symmetry axes can be of different orders. Let us consider this citing a 4-fold axis which includes rotations $1, \pi/2, \pi, 3\pi/2$ as an example. We add to it the translations t_1 and t_2 of a primitive unit cell. The following rotations result:

Rotation	Translation		
	t_1	t_2	$t_1 + t_2$
1	*1*	*1*	*1*
$\pi/2$	$\pi/2$	$3\pi/2$	$\pi/2$
π	π	π	π
$3\pi/2$	$3\pi/2$	$3\pi/2$	$3\pi/2$

It can be seen from the Table that a 4-fold axis passing through the vertex of a primitive cell generates a 4-fold axis in the centre of the cell and 2-fold axes in the middle of its edges.

Theorem 14. An inversion-rotation axis with a rotation angle α and translation t perpendicular to it generate the same inversion-rotation axis parallel to the generating one.

Decomposing the inversion-rotation axis $A_{\bar{\alpha}}$ into a rotation one A_α and an inversion in the centre of symmetry $\bar{1}$ we reduce the proof to the preceding one. Applying Theorem 14 to the inversion axis $\bar{1}$ we obtain a *corollary*: the centre of symmetry and translation t generate a new centre of symmetry displaced with respect to the given one in the direction of translation t by half its magnitude.

Theorem 15. An inversion-rotation axis with a rotation angle α and translation t that makes up angle β with the axis generate an inversion axis having the same rotation α parallel to the given one.

The proof is reduced to the preceding ones: decompose translation t into $t_\parallel$ and $t_\perp$: $A_{\bar{\alpha}1} = A_\alpha \cdot \bar{1} \cdot t_\parallel \cdot t_\perp = B_\alpha \cdot t_\parallel \cdot \bar{1} = B_{\bar{\alpha}} \cdot t_\parallel = B''_{\bar{\alpha}}$, and, using equations (9.8) and (9.9), obtain

$$AB' = \frac{t}{2} \frac{\sin \beta}{\cos (\alpha/2)}.$$

All the theorems of Secs. 3 and 6 are special cases of the multiplication of symmetry operations without translations. The addition of translations extends the number of generated symmetry elements. Thus, it was proved in Theorem 2 (Sec. 3) that intersecting symmetry planes m generate a rotation symmetry axis. It can be seen from the proofs of the preceding theorems that if the generating intersecting planes are the glide reflection planes, then the screw axes passing through the intersection of plane or the ones displaced with respect to it become the generated elements. The theorem on the intersec-

tion of symmetry axes also gives a diversity of solutions if the screw symmetry axes are taken into consideration.

The theorems and examples considered do not exhaust all the possible combinations of infinite symmetrical transformations, but they lucidly illustrate the great variety of these combinations and the principle of their derivation.

Sec. 10. 230 Space Groups of Symmetry

A space group of symmetry is the combination of all possible transformations of the symmetry of crystal structure. A space group of symmetry specifies the symmetry of crystal structure just as a point group of symmetry specifies the symmetry of the external form of a crystal and the symmetry of its macroscopic properties.

Several space groups correspond to each point group. In order to obtain the point group of a crystal from its space group of symmetry, it is necessary to mentally cancel all the translations, i.e. to turn the glide reflection planes into ordinary mirror reflection planes, the screw axes into ordinary rotation symmetry axes and to bring all the remaining symmetry elements to a single point.

A more complicated problem is the derivation of all the space groups from a point group. For this purpose, it is necessary to go over all the possible combinations of symmetry elements and the Bravais lattices. Thus, for instance, if a point group contains 3- and 2-fold axes, then it is necessary to try all the possible combinations of 3-, 3_1-, 3_2-, 2-, 2_1-fold axes and translations. Thus, the 230 continuous symmetry space groups of crystal space, or Fedorov's symmetry groups are obtained. Each of the groups satisfies conditions specified in the theory of groups, i.e. forms a mathematical group.

The 230 space groups were simultaneously derived in 1890-1894 by E. S. Fedorov and A. Schoenflies independently of each other.

The space groups are denoted by international symbols,Schoenflies symbols and Fedorov's symbols.

The international symbol of a space group is composed so as to make possible to obtain a full idea of the mutual arrangement of symmetry elements by the symbol itself, providing the basic theorems on the addition of infinite symmetry elements and the rules for writing down symbols as given in Table 10.1 are known.

In Schoenflies notation the space groups are denoted simply by the number of the group within a given class. The Schoenflies symbol does not determine the space group symmetry; it is necessary to resort to tables giving the juxtaposition of the Schoenflies and international symbols.

According to E. S. Fedorov, the space groups are denoted by numbers with indices *s*, *h*, *a*. Here *s* are symmorphous groups: paral-

Table 10.1

Rules for Writing down Symbols of Space Groups

System	Position			
	I	II	III	IV
Triclinic	Type of Bravais lattice	Available symmetry element		
Monoclinic		Available symmetry element		
		2 or 2_1 (and plane perpendicular to 2-fold axis if it is available)		
Rhombic		Plane perpendicular to, or axis parallel to *X* axis	*Y* axis	*Z* axis
Tetragonal Hexagonal		Axis of the highest order (and plane perpendicular to it)	Coordinate plane or axis	Diagonal plane or axis
Cubic		Coordinate planes or axes	3	Diagonal planes or axes

lel to the rotation axes of a point group in a space group there are arrays of simple or screw axes of the same order, parallel to planes *m* of a point group there are planes *m* or glide reflection planes in its space group. Similar symmetry elements intersect at a single point. *h* are hemisymmorphous groups: parallel to all rotation axes of the symmetry point group there are similar rotation or screw symmetry axes, but parallel to planes *m* of a point group in the space group there are only glide reflection planes. Similar axes intersect at a single point. *a* are asymmorphous groups: at least one set of symmetry axes of a space group parallel to the corresponding symmetry axes of a point group consists of screw axes alone (E. S. Fedorov, 1949).

In an international space group symbol, as in a point group symbol only the generating symmetry elements are included. The sequence of writing a symbol is of a decisive importance. In a space group symbol the first place always belongs to the Bravais lattice symbol. Next follow the generating symmetry elements, each in its strictly definite place (Table 10.1).

It is clear from the rules of writing symbols in the rhombic system and in the systems of the intermediate category why the coordinate and diagonal symmetry elements differ in such symbols of point groups as, for example, $4mm$ or $6mm$. From Theorems 8 and 9 (Sec. 9) it is evident that the addition of a translation to coordinate or diagonal symmetry elements is not equivalent. Therefore there is a distinction between these two possibilities in the point group symbol.

In symbols of the cubic system groups the digit 3 is always in the third position. It means the presence of four 3-fold axes imperative in this system.

The absence of a symmetry element in the appropriate position is denoted by digit 1.

Let us consider several examples.

Point Group. 2. According to Table 9.1 P- and I-Bravais cells are possible in the monoclinic system. Multiplication of the only symmetry operation 2 by translation t gives a screw axis $2_1 : 2 \cdot t = 2_1$. According to Theorem 10, the translations of P-cell in combination with 2-fold or 2_1-fold axes generate inserted axes of the same denomination, while according to Theorem 12, the translations of I-cell generate alternating 2- and 2_1-fold axes. Thus, three space groups: $P2$, $P2_1$, $I2$ are obtained. Since the 2_1 screw axes are neutral, all these space groups are also neutral. The 2-fold or 2_1-fold axis is polar. The space group $P2_1$ characterizes the structure of the Rochelle salt in a ferroelectric phase.

At temperatures of —18 °C or +24 °C there occurs the transition of the Rochelle salt from the monoclinic ferroelectric phase into the paraelectric rhombic phase characterized by space group $P2_12_12$. Fig. 10.1 shows these groups at standard orientation: the 2_1 screw axes are in the XY plane and are therefore shown by arrows.

To the symmetry point group 32 of quartz the following space groups belong accordingly:

$P321$	$P3_121$	$P3_221$
$P312$	$P3_112$	$P3_212$
	$R32$	

In the space groups listed in the first line the shortest translations in the basal plane are parallel to 2-fold axes, and make up 60° angles in the groups listed in the second line.

The $P3_121$ or $P3_221$ space group of the quartz structure can be right- or left-handed, this being manifested in the existence of enantiomorphous right- or left-handed quartz crystals (see Fig. 3.6) and in the availability rotation of the plane of polarization in these crystals. Such a structure has the low-temperature α-quartz; at a temperature higher than +573 °C quartz transforms into a high-temperature modification β, class 622. The right-handed α-quartz transforms into exactly the right-handed β-quartz ($P6_222$), and the left-handed ($P3_221$) into the left-handed ($P6_422$) (Fig. 10.2). The 2-fold axes lose their polarity.

The "International Tables" (1965) from which Fig. 10.2 was taken contain the diagrams and symbols of all the 230 space groups. The symbols given in the first edition ("old ones") of "International Tables" are slightly different from those adopted at present, the so-called "new" symbols. The figures are given with notation shown in Table 3. 1

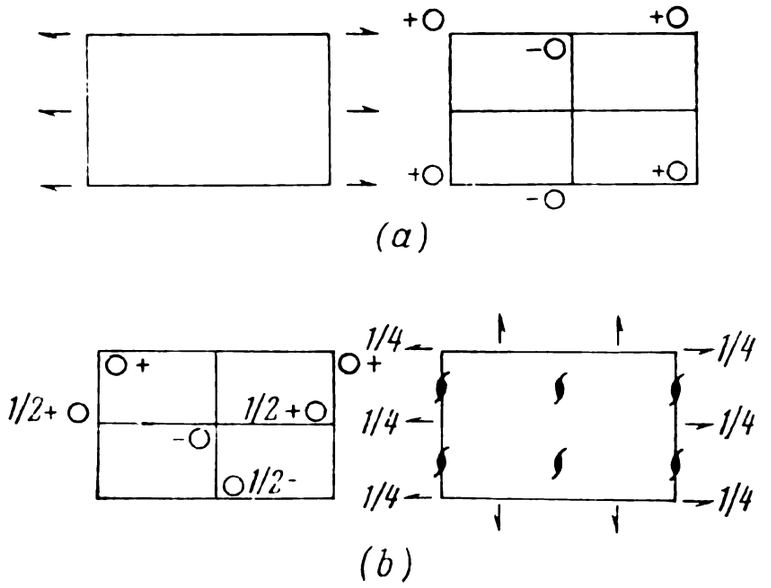


Fig. 10.1. Space groups $P2_1$ (a) and $P2_12_12$ (b) characterizing the changes in the Rochelle salt symmetry under phase transition

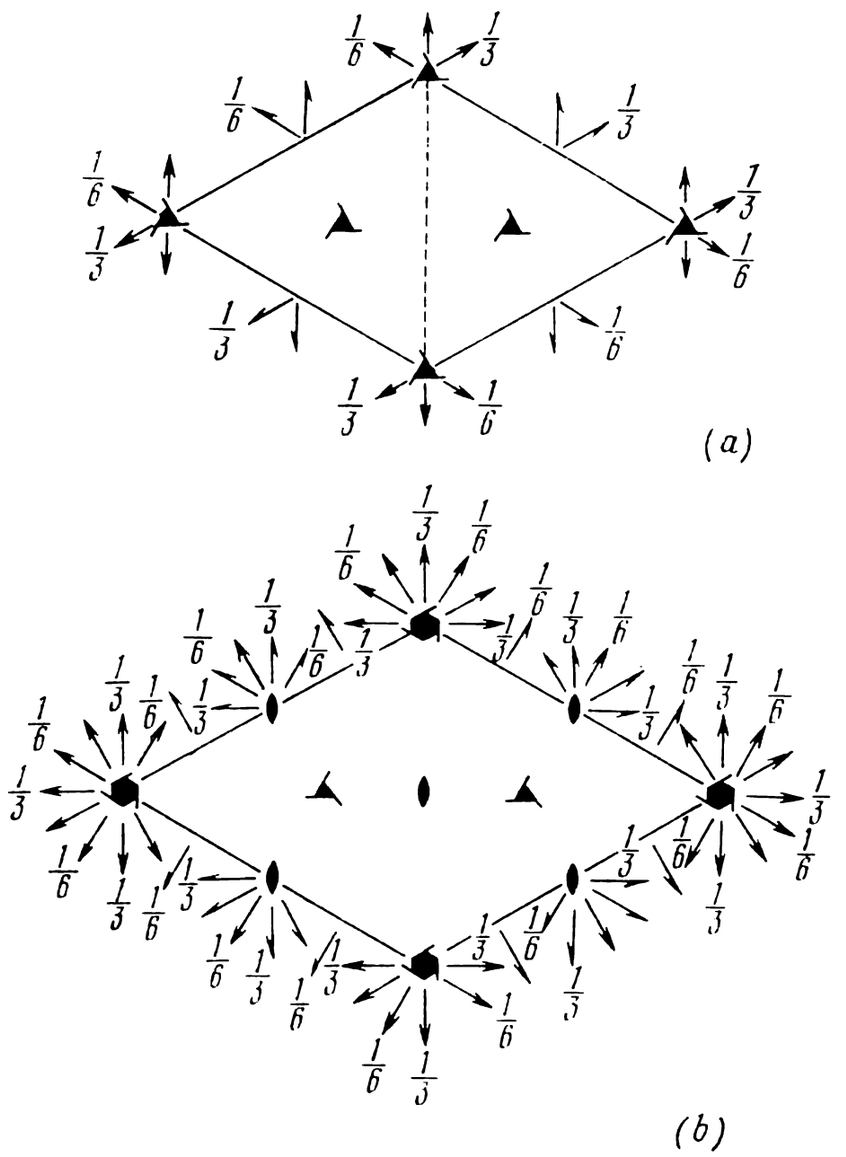


Fig. 10.2. Space groups $P3_121$ (a) and $R6_222$ (b) characterizing a change in the symmetry of quartz under phase transition

The "International Tables" contain, along with the diagrams of mutual arrangement of symmetry elements, the coordinates and diagrams of point symmetries for each space group. The set of points connected by the symmetry elements of the space group is a regular set of points. Point symmetry can be obtained from a single point by its repetition by means of all symmetry elements of the space group.

Sec. 11. Mutual Vector Basis and Reciprocal Lattice

Along with the principal covariant basis $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ a mutual vector basis is used consisting also of three vectors which we shall denote by the same letter $\boldsymbol{a}$ with different superscripts: $\boldsymbol{a}^1$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3$ and call them *contravariant base vectors* or *base vectors of a reciprocal lattice.* These vectors are defined as the solution of the following set of 9 linear equations connecting them with the ordinary or covariant base vectors:

$$\boldsymbol{a}_1\cdot\boldsymbol{a}^1=1,\quad \boldsymbol{a}_2\cdot\boldsymbol{a}^1=0,\quad \boldsymbol{a}_3\cdot\boldsymbol{a}^1=0,$$
$$\boldsymbol{a}_1\cdot\boldsymbol{a}^2=0,\quad \boldsymbol{a}_2\cdot\boldsymbol{a}^2=1,\quad \boldsymbol{a}_3\cdot\boldsymbol{a}^2=0,$$
$$\boldsymbol{a}_1\cdot\boldsymbol{a}^3=0,\quad \boldsymbol{a}_2\cdot\boldsymbol{a}^3=0,\quad \boldsymbol{a}_3\cdot\boldsymbol{a}^3=1.$$

If Kronecker's symbol is introduced

$$\delta_\alpha^\beta=\begin{cases}1 & \text{for}\quad \beta=\alpha,\\ 0 & \text{for}\quad \beta\neq\alpha,\end{cases}\tag{11.1}$$

the system of equations can be rewritten in a shorter form:

$$\boldsymbol{a}_\alpha\cdot\boldsymbol{a}^\beta=\delta_\alpha^\beta\quad(\alpha,\beta=1,2,3).\tag{11.2}$$

System (11.2) shows that any contravariant base vector (let us say, $\boldsymbol{a}^1$) is perpendicular to the two covariant base vectors with other numbers (in our example $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$) and makes up an acute angle with a covariant base vector ($\boldsymbol{a}_1$) of the same number. Indeed, if the scalar product of two vectors is zero, they are mutually perpendicular, but if it is positive, the angle between them is smaller than the right one. Since vector $\boldsymbol{a}^1$ is perpendicular to both vector $\boldsymbol{a}_2$ and vector $\boldsymbol{a}_3$ it is collinear with their vector product: $\boldsymbol{a}^1 = m\boldsymbol{a}_2\times\boldsymbol{a}_3$, where m is a certain number unknown to us. In order to find it, we insert $\boldsymbol{a}^1$ from the expression $m\boldsymbol{a}_1(\boldsymbol{a}_2\cdot\boldsymbol{a}_3)=1$ into product $\boldsymbol{a}_1\cdot\boldsymbol{a}^1$. Note that the volume of a unit cell constructed on vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ equals

$$v=\boldsymbol{a}_1\cdot(\boldsymbol{a}_2\times\boldsymbol{a}_3)=\boldsymbol{a}_2\cdot(\boldsymbol{a}_3\times\boldsymbol{a}_1)=\boldsymbol{a}_3\cdot(\boldsymbol{a}_1\times\boldsymbol{a}_2).\tag{11.3}$$

Hence $m=1/v$. Having calculated $\boldsymbol{a}^2$ and $\boldsymbol{a}^3$ in the same way we obtain

$$\boldsymbol{a}^1=\frac{\boldsymbol{a}_2\times\boldsymbol{a}_3}{v},\quad \boldsymbol{a}^2=\frac{\boldsymbol{a}_3\times\boldsymbol{a}_1}{v},\quad \boldsymbol{a}_3=\frac{\boldsymbol{a}_1\times\boldsymbol{a}_2}{v}.\tag{11.4}$$

Equalities (11.4) show that the base vectors of a reciprocal lattice, $\boldsymbol{a}^1$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3$, are directed along the perpendiculars to the coordinate planes of crystal lattice. Their lengths, as will be shown later, are equal to the converse interplanar distances of the coordinate plane nets of the lattice.

Let us calculate the scalar triple product of the contravariant base vectors $\boldsymbol{a}^1 \cdot (\boldsymbol{a}^2 \times \boldsymbol{a}^3)$. By using the well-known formula of a binary vector product $(\boldsymbol{A} \times \boldsymbol{B}) \times \boldsymbol{C} = (\boldsymbol{A} \cdot \boldsymbol{C}) \cdot \boldsymbol{B} - (\boldsymbol{B} \cdot \boldsymbol{C}) \cdot \boldsymbol{A}$ we perform the following calculation: $\boldsymbol{a}^2 \times \boldsymbol{a}^3 = (1/v^2)(\boldsymbol{a}_3 \times \boldsymbol{a}_1) \times (\boldsymbol{a}_1 \times \boldsymbol{a}_2) = (1/v^2)\{[\boldsymbol{a}_3 \cdot (\boldsymbol{a}_1 \times \boldsymbol{a}_2)]\boldsymbol{a}_1 - [\boldsymbol{a}_1(\boldsymbol{a}_1 \times \boldsymbol{a}_2)]\boldsymbol{a}_3\} = (1/v)\boldsymbol{a}_1$, since the second term is zero. Then, having noted that $\boldsymbol{a}^1 \cdot \boldsymbol{a}_1 = 1$, we finally find

$$\boldsymbol{a}^1 \cdot (\boldsymbol{a}^2 \times \boldsymbol{a}^3) = 1/v. \tag{11.5}$$

It follows that the contravariant base vectors $\boldsymbol{a}^1$, $\boldsymbol{a}^2, \boldsymbol{a}^3$ are noncoplanar (since their mixed product is not equal to zero) and form a right-hand triplet (since the product is positive).

Having noted that the covariant and contravariant base vectors enter basic equations (11.2) quite in a symmetric way, we can, by analogy with (11.4), directly write down the equations expressing the covariant base vectors in terms of the contravariant ones:

$$\boldsymbol{a}_1 = v\boldsymbol{a}^2 \times \boldsymbol{a}^3, \quad \boldsymbol{a}_2 = v\boldsymbol{a}^3 \times \boldsymbol{a}^1, \quad \boldsymbol{a}_3 = v\boldsymbol{a}^1 \times \boldsymbol{a}^2 \tag{11.6}$$

(we have already obtained the first formula in calculating the mixed product of the contravariant base vectors).

A parallelepiped constructed on the contravariant base vectors $\boldsymbol{a}^1$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3$ is called a *crystallographic cell of the reciprocal lattice.* If the crystallographic cell of the direct lattice coincides with the unit cell, the crystallographic cell of the reciprocal lattice is also called a unit cell. By unrestricted repetition of this cell in the three space directions a lattice can be constructed from these parallelepipeds. It is called a *reciprocal crystal lattice*; it is widely used in the theory of X-ray of crystal analysis structure and in solid-state physics. Therefore the contravariant base vectors are often called the *base vectors of the reciprocal lattice.*

The base vectors of the reciprocal lattice, i.e. contravariant base vectors, $\boldsymbol{a}^1$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3$, as any vectors in general, can be referred to the principal (covariant) basis $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$:

$$\boldsymbol{a}^1 = g^{11}\boldsymbol{a}_1 + g^{12}\boldsymbol{a}_2 + g^{13}\boldsymbol{a}_3,$$
$$\boldsymbol{a}^2 = g^{21}\boldsymbol{a}_1 + g^{22}\boldsymbol{a}_2 + g^{23}\boldsymbol{a}_3,$$
$$\boldsymbol{a}^3 = g^{31}\boldsymbol{a}_1 + g^{32}\boldsymbol{a}_2 + g^{33}\boldsymbol{a}_3.$$

Superscripts at the expansion coefficients, g, have the following meaning: the first one is for the number of the resolved vector, the second one for that of the resolving one; (they are not to be confused with

powers!). With the use of letter-indices and the notation for summation the three expansions can be written down in a shorter form:

$$\boldsymbol{a}^{\alpha} = \sum_{\beta=1}^{3} g^{\alpha\beta}\boldsymbol{a}_{\beta} \quad (\alpha = 1, 2, 3),$$

and they can be written in a still more laconic form with the aid of the Einstein summation convention

$$\boldsymbol{a}^{\alpha} = g^{\alpha\beta}\boldsymbol{a}_{\beta}. \tag{11.7}$$

The need for summation is indicated here by the following: β—the index of summation—is written twice: as a superscript and as a subscript; and when two identical Greek indices occur in a "monomial", one as a superscript and the other as a subscript, we have not a monomial but rather a sum of monomials in which the summation index has consecutive meanings, 1, 2, 3 (the cases when indices have other values will be specified later on).

Expansion coefficients, $g^{\alpha\beta}$ are called *contravariant components of a metric tensor*. To elucidate their meaning, we scalarly multiply the right- and left-hand sides of equalities (11.7) by a certain contravariant base vector $\boldsymbol{a}^{\gamma}$. Knowing that $\boldsymbol{a}_{\beta}\cdot\boldsymbol{a}^{\gamma} = \delta_{\beta}^{\gamma}$, we obtain

$$\boldsymbol{a}^{\alpha}\cdot\boldsymbol{a}^{\gamma} = g^{\alpha\gamma}. \tag{11.8}$$

Thus the contravariant components of a metric tensor are equal to the scalar products of corresponding contravariant base vectors. Since the scalar multiplication of vectors is commutative, i.e. since its results do not depend on the sequence of the factors, the components do not change under permutation of indices:

$$g^{\alpha\gamma} = g^{\gamma\alpha}. \tag{11.9}$$

Let us now consider the expansion of the base lattice vectors, $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, in the base vectors of the reciprocal lattice $\boldsymbol{a}^1$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3$:

$$\boldsymbol{a}_1 = g_{11}\boldsymbol{a}^1 + g_{12}\boldsymbol{a}^2 + g_{13}\boldsymbol{a}^3,$$
$$\boldsymbol{a}_2 = g_{21}\boldsymbol{a}^1 + g_{22}\boldsymbol{a}^2 + g_{23}\boldsymbol{a}^3,$$
$$\boldsymbol{a}_3 = g_{31}\boldsymbol{a}^1 + g_{32}\boldsymbol{a}^2 + g_{33}\boldsymbol{a}^3$$

or, which is just the same:

$$\boldsymbol{a}_{\alpha} = g_{\alpha\beta}\boldsymbol{a}^{\beta}. \tag{11.10}$$

The coefficients of this expansion, $g_{\alpha\beta}$ are called *covariant components of a metric tensor*. They are equal to the scalar products of the corresponding base vectors of a crystal lattice:

$$g_{\alpha\gamma} = \boldsymbol{a}_{\alpha}\cdot\boldsymbol{a}_{\gamma}. \tag{11.11}$$

Obviously they do not change under the permutation of indices:

$$g_{\alpha\gamma} = g_{\gamma\alpha}. \tag{11.12}$$

The sets of numbers $g_{\alpha\beta}$ and $g^{\alpha\beta}$ are matrices; the comparison of equalities (11.7) and (11.10) shows that these matrices are mutually reciprocal. If we denote, $\| g_{\alpha\beta} \| = G$, then $\| g^{\alpha\beta} \| = G^{-1}$ and the following relation

$$g_{\alpha\beta} g^{\beta\gamma} = \delta_{\alpha}^{\gamma} \tag{11.13}$$

will hold.

It follows from (11.11) that the covariant components of the metric tensor $g_{\alpha\beta}$ are completely determined by the cell parameters, by the length of the edges and the angles between the edges. If the lengths of the edges are denoted a, b, c, and the angles between them α, β, γ (see Fig. 1.15), then

$$G = \begin{Vmatrix} a^2 & ab\cos\gamma & ca\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ca\cos\beta & bc\cos\alpha & c^2 \end{Vmatrix}. \tag{11.14}$$

On the other hand, knowing the covariant components of the metric tensor, it is not difficult to calculate the cell parameters

$$a = \sqrt{g_{11}}, \quad b = \sqrt{g_{22}}, \quad c = \sqrt{g_{33}},$$

$$\alpha = \arccos \frac{g_{23}}{\sqrt{g_{22}g_{33}}}, \quad \beta \quad \arccos \frac{g_{31}}{\sqrt{g_{33}g_{11}}}, \tag{11.15}$$

$$\gamma = \arccos \frac{g_{12}}{\sqrt{g_{11}g_{22}}}$$

As it is proved in Sec. 16, the volume of a unit cell equals $v = \sqrt{\det G}$; comparing it with (11.14) we obtain

$$v = abc\omega,$$

$$\omega = \sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}. \tag{11.16}$$

The contravariant components of the metric tensor form a matrix

$$G^{-1} = \begin{Vmatrix} a^{*2} & a^*b^*\cos\gamma^* & c^*a^*\cos\beta^* \\ a^*b^*\cos\gamma^* & b^{*2} & b^*c^*\cos\alpha^* \\ c^*a^*\cos\beta^* & b^*c^*\cos\alpha^* & c^{*2} \end{Vmatrix}, \tag{11.17}$$

in which a^*, b^*, c^* are the edge lengths of a reciprocal lattice cell and α^*, β^*, γ^* are the angles between them. They are calculated from the contravariant components of the metric tensor with the aid of equalities fully similar to (11.5) and are connected with the

parameters of the crystal lattice cell by relations

$$a^* = \frac{\sin\alpha}{a\omega}, \quad b^* = \frac{\sin\beta}{b\omega}, \quad c^* = \frac{\sin\gamma}{c\omega},$$

$$\cos\alpha^* = \frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma}, \quad \cos\beta^* = \frac{\cos\gamma\cos\alpha - \cos\beta}{\sin\gamma\sin\alpha}, \tag{11.18}$$

$$\cos\gamma^* = \frac{\cos\alpha\cos\beta - \cos\gamma}{\sin\alpha\sin\beta}.$$

Matrices G and G^{-1} for all the 14 Bravais lattices (with the conventional choice of a unit cell in each of them) are given in Appendix B.

A parallelepiped constructed on the contravariant base vectors $\boldsymbol{a}^1$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3$ is called the *elementary cell of a reciprocal lattice*; the reciprocal lattice is constructed of such parallelepipeds.

Each point of the reciprocal lattice corresponds in the reciprocal space to the plane of the direct lattice. To an infinite family of parallel planes in space there corresponds in a reciprocal space an infinite family of points situated in a direction perpendicular to the planes. The initial and reciprocal lattices are mutually conjugate and have identical point symmetries (but their space groups are, in general, different).

Periodic distribution of the reflecting capacity of a crystal with respect to X-rays is described with the aid of a reciprocal lattice. The fundamental equation of the X-ray diffraction in crystals (the Wulff-Bragg formula) defines the relation between the wavelength λ, interplanar distance d for a series of lattice planes, parallel to the reflecting plane, the n-th order of the diffraction spectrum from this series of planes and the angle of incidence of the wave on a crystal

$$2d\sin\theta = n\lambda. \tag{11.19}$$

Here θ is the angle supplemental to the angle of incidence.

The interplanar distances between coordinate planes (100), (010) and (001) are reciprocals of the lengths of the edges of the reciprocal lattice cell, a^*, b^*, and c^*, and are defined by equations (11.18); in a general case the interplanar distance is defined by equation (15.30).

The direction of a reciprocal lattice vector $\boldsymbol{r}^*$ coincides with the direction of the reflection of X-rays from a series of parallel planes of the direct lattice, while an n-th point in a reciprocal lattice row corresponds to a reflection of the n-th order from this series of planes. Each point of a reciprocal lattice corresponds to the direction of a beam of X-rays diffracted by a series of parallel lattice planes.

Sec. 12. Indexing of Directions and Planes in Crystals

In Sec. 1 it was shown that it is possible to introduce for each crystal a crystallographic system of coordinates, X, Y, Z, constructed on base vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, which coincide with the edges of a unit

cell. Since vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ are non-coplanar, any vector $\boldsymbol{l}$ can be uniquely represented as their linear combination

$$\boldsymbol{l} = l^1\boldsymbol{a}_1 + l^2\boldsymbol{a}_2 + l^3\boldsymbol{a}_3. \tag{12.1}$$

Numbers l^1, l^2, l^3 are called the components of vector $\boldsymbol{l}$ with respect to the basis $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$.

In Einstein's notation

$$\boldsymbol{l} = l^\alpha \boldsymbol{a}_\alpha. \tag{12.2}$$

Let vector $\boldsymbol{l} = l^\alpha \boldsymbol{a}_\alpha$ with integral components l^1, l^2, l^3 determine the crystallographic direction. If the components have a common integer factor n, we can take into consideration a vector of the same direction but n times shorter

$$\boldsymbol{l}' = \boldsymbol{l}/n = (l^1/n)\,\boldsymbol{a}_1 + (l^2/n)\,\boldsymbol{a}_2 + (l^3/n)\,\boldsymbol{a}_3,$$

and its components will also be integers. Hence let us agree that the division by all the common factors has already been done. In this case components l^1, l^2, l^3 written as $[l^1 l^2 l^3]$, will be *Miller indices* of the given crystallographic direction, i.e. of any straight line with a direction parallel to the given vector. As was pointed out in Sec. 1, indices of a row are written in square brackets, for example, the symbols of coordinate axes are denoted [100], [010], [001].

The set of directions, which can symmetrically coincide with each other under symmetric transformations inherent in the given symmetry class, is written in French quotes; for instance, the set of cube edges ⟨100⟩, of spatial diagonals of a cube ⟨111⟩, of cube face diagonals ⟨110⟩. If some of the l^α numbers are negative, the minus sign is written over the number, for example $\langle 1\bar{1}0 \rangle$ (it is read one, minus one, 0). If numbers greater than 9 occur in the Miller indices, the latter are separated from each other by points, to avoid misunderstanding, but such crystallographic directions very rarely occur in practice.

When a unit cell is non-primitive, not each vector plotted from the origin to the lattice point will have integral components, but it is possible to find for any crystallographic direction its determining vector with integral components: a pointsymbol in the centre of the unit cell [[1/2 1/2 1/2]], but a row plotted through it (spatial diagonal of a cube) can be specified by symbol [111], since it also passes through the [[111]] point.

It is natural to specify any set of parallel planes by a vector perpendicular to them; if they are crystallographic ones, i.e. contain at least three crystal lattice points not situated on a single straight line, it would be desirable to specify them by a vector with integer components. Let us select from a set of parallel crystallographic planes a plane that intersects crystallographic axes at the crystal lattice points but does not pass through the origin. The position

of the plane is unambiguously determined by integer intercepts which it cuts on the crystallographic coordinate axes (Fig. 12.1). There are three cases possible:

(1) three such intercepts are available—the plane is parallel to none of the coordinate axes;

(2) the plane is parallel to one of the axes, it cuts off integer intercepts on two other axes;

(3) the plane is parallel to two axes, an intercept is cut off only on the third one.

Let us consider the first case. Vectors

$$\boldsymbol{p}_{(1)} = p^1\boldsymbol{a}_1 \quad \boldsymbol{p}_{(2)} = p^2\boldsymbol{a}_2, \quad \boldsymbol{p}_{(3)} = p^3\boldsymbol{a}_3, \tag{12.3}$$

connecting the origin with the points of intersection of axes with the plane are integers. The lengths of vectors

$$\boldsymbol{q}_{(1)} = \boldsymbol{p}_{(1)} - \boldsymbol{p}_{(3)} \text{ and}$$
$$\boldsymbol{q}_{(2)} = \boldsymbol{p}_{(2)} - \boldsymbol{p}_{(3)} \tag{12.4}$$

are also integers, they lie in the crystallographic plane with which we are concerned, and their vector product is perpendicular to it. It is convenient to divide the latter by the unit cell volume v, this will of course have no effect on the direction, and to choose such a sequence of factors that the direction is an external normal to the plane (with the origin located inside the crystal).

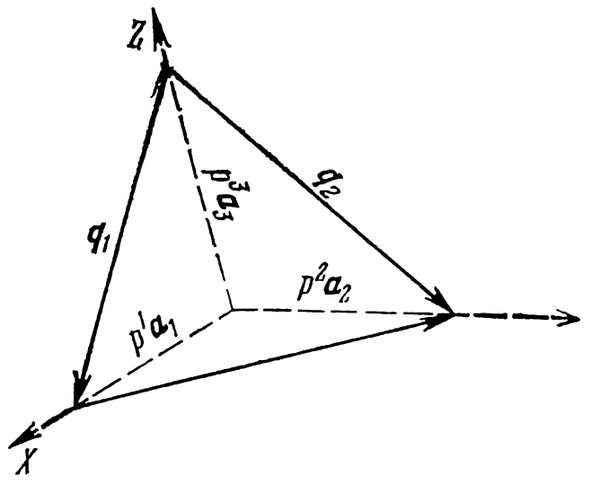


Fig. 12.1. To the explanation of the symbol of a plane

Thus, a face is characterized by a vector perpendicular to it

$$\boldsymbol{n} = \frac{1}{v}(\boldsymbol{q}_{(1)} \times \boldsymbol{q}_{(2)}). \tag{12.5}$$

Let us calculate it. Substituting into (12.5) the expressions for $\boldsymbol{q}_{(1)}$ and $\boldsymbol{q}_{(2)}$ from (12.4) and replacing vectors $\boldsymbol{p}_{(1)}$, $\boldsymbol{p}_{(2)}$ and $\boldsymbol{p}_{(3)}$ by expressions (12.3), we obtain

$$\boldsymbol{n} = \frac{1}{v}(p^1\boldsymbol{a}_1 - p^3\boldsymbol{a}_3) \times (p^2\boldsymbol{a}_2 - p^3\boldsymbol{a}_3).$$

We perform the multiplication term-by-term:

$$\boldsymbol{n} = \frac{1}{v}(p^1p^2\boldsymbol{a}_1 \times \boldsymbol{a}_2 + p^3p^1\boldsymbol{a}_3 \times \boldsymbol{a}_1 + p^2p^3\boldsymbol{a}_2 \times \boldsymbol{a}_3).$$

Now let us notice that the division of the vector products of the base vectors by v will produce base vectors of a reciprocal lattice

$$\boldsymbol{n} = p^2p^3\boldsymbol{a}^1 + p^3p^1\boldsymbol{a}^2 + p^1p^2\boldsymbol{a}^3. \tag{12.6}$$

Denoting $n_{(1)} = p^2p^3$, $n_2 = p^3p^1$, $n_3 = p^1p^2$, we obtain finally

$$\boldsymbol{n} = n_1\boldsymbol{a}^1 + n_2\boldsymbol{a}^2 + n_3\boldsymbol{a}^3 = n_\alpha\boldsymbol{a}^\alpha. \tag{12.7}$$

Numbers n_1, n_2, n_3 are the components of vector $\boldsymbol{n}$ with respect to the mutual basis $\boldsymbol{a}^1$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3$. Being the products of integers they are also integers.

Now we consider the second case. Let, for instance, a crystallographic plane be parallel to the X axis, while the lattice points at which it intersects axes Y and Z are connected with the origin by vectors with integral lengths

$$\boldsymbol{p}_{(2)} = p^{(2)}\boldsymbol{a}_2, \quad \boldsymbol{p}_{(3)} = p^{(3)}\boldsymbol{a}_3. \tag{12.8}$$

Then the plane is parallel to vectors $\boldsymbol{a}_{(1)}$ and $\boldsymbol{q} = \boldsymbol{p}_2 - \boldsymbol{p}_3$, while the vector of a perpendicular to it can be determined from the expression

$$\boldsymbol{n} = \frac{1}{v}\boldsymbol{a}_1 \times \boldsymbol{q}. \tag{12.9}$$

Performing the same calculations as in the first case we find

$$\boldsymbol{n} = p^{(3)}\boldsymbol{a}^{(2)} + p^{(2)}\boldsymbol{a}^{(3)}. \tag{12.10}$$

Also, $\boldsymbol{n} = n_\alpha\boldsymbol{a}^\alpha$, where

$$n_1 = 0, \quad n_2 = p^{(3)} \quad n_3 = p^{(2)}. \tag{12.11}$$

Finally, we shall discuss a crystallographic plane parallel to the X and Y axes and intersecting the Z axis in its positive part. Since it is parallel to vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$, we can at once write

$$\boldsymbol{n} = \frac{1}{v}\boldsymbol{a}_1 \times \boldsymbol{a}_2 = \boldsymbol{a}^3. \tag{12.12}$$

In the expression $\boldsymbol{n} = n_\alpha\boldsymbol{a}^\alpha$ the components $n_1 = n_2 = 0$, $n_3 = 1$ (if the plane intersected the Z axis in its negative half, then it would be necessary to reverse the order of the factors, and $\boldsymbol{n} = -\boldsymbol{a}^3$ and $n_3 = -1$ accordingly).

Thus, a vector of the normal to the possible or real crystal face can be always chosen so that it will have integral components with respect to the basis of a reciprocal lattice. These components are *Miller indices of a face (plane)* (see Sec. 1); they are written in the same way as the direction (edge) indices, but in parentheses $(n_1n_2n_3)$ instead of in square brackets. If they have a common factor, they should be divided by it*. Three indices in parentheses are called the *symbol of face (plane)*.

The face Miller indices are inversely proportional to the components of vectors drawn from the origin to the points of intersection

* In the problems of X-ray structure analysis this is not always permissible.

of the face with the coordinate axes. In fact, when a given face intersects all the three axes, it follows from (12.6) that

$$n_1 : n_2 : n_3 = \frac{1}{p^{(1)}} : \frac{1}{p^{(2)}} : \frac{1}{p^{(3)}}, \tag{12.13}$$

and when it intersects two axes, let us say, Y and Z, it follows from (12.11) that

$$n_2 : n_3 = \frac{1}{p^{(2)}} : \frac{1}{p^{(3)}}. \tag{12.14}$$

The coordinate planes are specified by symbols: (100)—YOZ, (010)—ZOX, and (001)—XOY.

So we have introduced two vector bases: the lattice basis $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ and the reciprocal lattice basis $\boldsymbol{a}^1$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3$. It was shown that vector $\boldsymbol{l}$ specifying the crystallographic direction can be chosen so that its components l^1, l^2, l^3 with respect to the lattice basis are integers, and the vector of a normal to the crystallographic plane $\boldsymbol{n}$ be chosen so that its components n_1, n_2, n_3 are integers with respect to the reciprocal lattice basis. It is certainly possible to resolve vector $\boldsymbol{l}$ into the base vectors of the reciprocal lattice, and vector $\boldsymbol{n}$ into the base vectors of the direct lattice, but then the components would not be integers and the crystallographic value of a given direction or a given plane would be lost. Therefore it is necessary to know how to choose a basis which would be convenient for specifying a crystallographic object.

In proving the Miller indices for crystallographic planes to be integers, we proceeded from the idea of the crystal lattice. Before the appearance of X-ray structure analysis and experimental proofs of the discreteness of crystal structure, the indexing of crystal faces was based on the law of the rationality of parameters (the law of integral relations) formulated by Haüy in 1781. Along with the law of the constancy of angles the law of Haüy is the basic empirical law of crystallography; it recognizes the regularity of the arrangement of faces on a crystal polyhedron and explains the reasons for the appearance of different particular faces on crystals.

The law of the rationality of parameters states: the dual ratios of intercepts, cut off on the three edges of a crystal, chosen as the coordinate axes (a) by any face of the crystal and (b) by a certain face chosen as the unit one, are equal to the ratios between small integers.

Let us choose three non-parallel faces of crystal polyhedron to be the coordinate planes, and the edges at which these faces intersect, to be the coordinate axes. Let us choose still another face, the so-called *unit* face. The unit face, not parallel to any of the coordinate faces, cuts off the intercepts OA, OB, OC, the so-called *parameters of the face* on the coordinate axes. According to the law of the rationality

of parameters, for any other face of the crystal that cuts off intercepts OA', OB', OC' on the coordinate axes, the dual ratio equals

$$\frac{OA}{OA'} : \frac{OB}{OB'} : \frac{OC}{OC'} = m : n : p, \tag{12.15}$$

where m, n, p are integers, mostly not exceeding 5. Faces for which the dual ratio of parameters is irrational are impossible for the crystals. If the ratios of parameters are mutually simple and integral but large (larger than 5), a face is possible but highly improbable.

The Haüy law is as important for crystallography as the Dalton law of multiple ratios is important for chemistry. According to the Dalton law of multiple ratios, only those compounds of chemical elements are possible in which elements are in integral ratios. According to the Haüy law of integers, a crystal polyhedron can have only such faces for which the dual ratios of intercepts cut off by a given face and a certain "unit" face are equal to the ratios of small integers.

Although the law of rational parameters was formulated only on the basis of the study of external forms of crystals, and at the time when only vague ideas were made concerning the structure of crystals appeared, a quarter of a century before the Dalton law, it was in essence the first numerical law defining the atomic-molecular structure of a substance.

Indeed, the law of the rational parameters, its meaning, can be easily and simply explained now, when it is known that particles in a crystal are arranged in orderly regular rows and that any crystal edge corresponds to a row of particles in the lattice. If any three edges of a crystal are chosen as the axes of coordinates, it is equivalent to three non-coplanar translations in the lattice being taken as the axes. Since any crystal face corresponds to a plane grid of the lattice, it should also pass through the points on axes X, Y, Z.

In essence, the sense of the Haüy law is that crystal faces always correspond to the plane nets of a crystal lattice, while crystal edges always correspond to the point rows of the lattice. Besides, real crystal edges correspond, as a rule, to plane nets with the greatest reticular density; this explains the fact that the indices of faces are not only integers but also small numbers.

This interpretation of the law is easily given now, when the lattice structure of crystals has been experimentally proved and well studied. A much more difficult road, however, was passed historically: from the observation of the external shapes of crystal polyhedrons, from the measurement of relative slopes of crystal faces to the first guesses on the periodic structure of crystals to the speculative theories of the crystal structure which were only later proved experimentally. The first concepts of the regular crystal structure were

suggested on the basis of the law of integer ratios. The study of the symmetric polyhedral forms of crystals resulted in the understanding of the proportionality of their structure.

The law of rational parameters holds even if the coordinate axes, chosen along the edges of a crystal polyhedron do not correspond to the edges of a unit cell. These edges should anyway be parallel to some rows of points in the lattice, while the distance between them is inevitably divided into equal intercepts by the sets of parallel planes to which any crystal face is parallel.

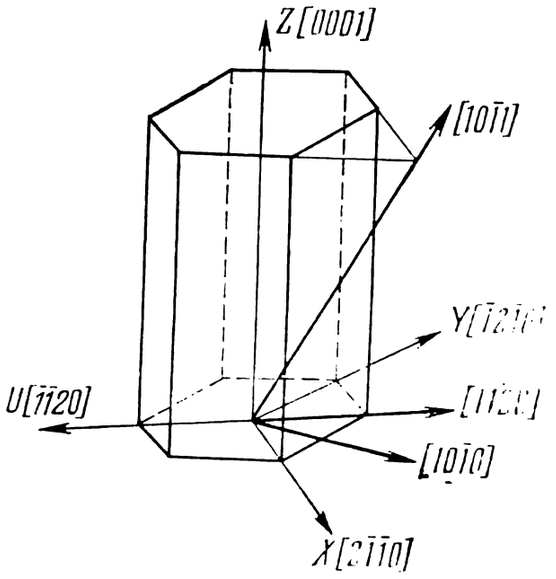


Fig. 12.2. Symbols of the principal directions in a hexagonal cell

It follows from the Haüy law, for instance, that any crystal face and any point plane in a crystal lattice can be specified by three small integers, if the directions of three crystal edges are chosen as the coordinate axes and the intercepts cut off on the axes by a crystal face are taken to be the units of measurement along these axes.

Crystallographic planes and directions in any crystal can be specified by the Miller indices. However, crystallographers do not use the Miller indices relating to the hexagonal system of coordinates, preferring the Bravais indices instead*. This is done so as to specify the symmetrically equivalent planes and directions by somewhat "similar" sets of indices, while the Miller indices, when referred to the hexagonal system of coordinates, do not satisfy this aim. Thus, in the hexagonal sets of axes the vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and $-\boldsymbol{a}_1$ $-\boldsymbol{a}_2$ define the symmetrically equivalent directions, while the Miller indices for two of them, [100] and [010], differ essentially from the indices for the third direction [$\bar{1}\bar{1}$0].

A four-axes system of coordinates is used to completely reveal the symmetry of hexagonal crystals: axis U directed along the vector $-\boldsymbol{a}_1 - \boldsymbol{a}_2$ is introduced in the basal plane in addition to the axes X and Y directed along $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ respectively. Vector $\boldsymbol{a}_3$ and correspondingly axis Z remain in the direction of the principal symmetry axis (Fig. 12.2). The crystallographic planes and directions are now specified by the orientation with respect to all the four axes and correspondingly by four indices which are called the *Bravais indices*. The sum of the first three Bravais indices is always zero.

* For specifying crystals of the trigonal system the Miller indices are sometimes used, but they are then referred to the rhombohedral system of coordinates and not to the hexagonal one (see Sec. 13).

The Bravais indices for the crystallographic direction $\boldsymbol{l}$ are the components of the expansion of vector $\boldsymbol{l}$ into four vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $-\boldsymbol{a}_1$, $-\boldsymbol{a}_2$, $\boldsymbol{a}_3$ provided that the sum of the first three components is zero. The method of changing from the usual vector notation to the Bravais indices follows from this definition. The vector of crystallographic direction

$$\boldsymbol{l} = l^1\boldsymbol{a}_1 + l^2\boldsymbol{a}_2 + l^3\boldsymbol{a}_3 \tag{12.16}$$

(l^1, l^2, l^3 are integers) can be written thus

$$\boldsymbol{l} = l^1\boldsymbol{a}_1 + l^2\boldsymbol{a}_2 + 0\,(-\boldsymbol{a}_1 - \boldsymbol{a}_2) + l^3\boldsymbol{a}_3.$$

Numbers l^1, l^2, 0, l^3 differ from the Bravais indices only in that the sum of the first three numbers is not zero. Let us add to vector $\boldsymbol{l}$ vector $\boldsymbol{m} = m\boldsymbol{a}_1 + m\boldsymbol{a}_2 + m\,(-\boldsymbol{a}_1 - \boldsymbol{a}_2) = 0$. Evidently

$$\boldsymbol{l} + \boldsymbol{m} = (l^1 + m)\,\boldsymbol{a}_1 + (l^2 + m)\,\boldsymbol{a}_2 + m\,(-\boldsymbol{a}_1 - \boldsymbol{a}_2) + l^3\boldsymbol{a}_3 = \boldsymbol{l}.$$

Let us take $m = -(l^1 + l^2)/3$, then the sum of the first three indices will be zero as was to be expected. For the indices to be integers, we multiply all the components by 3. Thus, for the crystallographic direction

$$\boldsymbol{l} = l^1\boldsymbol{a}_1 + l^2\boldsymbol{a}_2 + l^3\boldsymbol{a}_3$$

while the Bravais indices are

$$[2l^1 - l^2.\quad 2l^2 - l^1.\quad -l^1 - l^2.3l^3]. \tag{12.17}$$

Should the Bravais indices have a common factor, it must certainly be cancelled out. By means of the Bravais indices of the crystallographic direction $(r^1r^2r^3r^4)$ the vector $\boldsymbol{l}$ specifying it can easily be found. By definition: $\boldsymbol{l} = r^1\boldsymbol{a}_1 + r^2\boldsymbol{a}_2 + r^3\,(-\boldsymbol{a}_1 - \boldsymbol{a}_2) + r^4\boldsymbol{a}_3$. Grouping the similar terms, we obtain

$$\boldsymbol{l} = (r^1 - r^3)\,\boldsymbol{a}_1 + (r^2 - r^3)\,\boldsymbol{a}_2 + r^4\boldsymbol{a}_3, \tag{12.18}$$

thus solving the problem.

The Bravais indices for symmetrically equivalent directions are really very much alike. For example, axes X, Y and U are specified by symbols $[2\bar{1}\bar{1}0]$, $[\bar{1}2\bar{1}0]$ and $[\bar{1}\bar{1}20]$ respectively (see Fig. 12.2).

The Bravais indices for crystallographic planes are the expansion coefficients of the vector of a perpendicular to a crystallographic plane $\boldsymbol{n}$ in terms of four vectors

$$\frac{2}{3}\boldsymbol{a}^1 - \frac{1}{3}\boldsymbol{a}^2,\quad \frac{2}{3}\boldsymbol{a}^2 - \frac{1}{3}\boldsymbol{a}^1,\quad -\frac{1}{3}\boldsymbol{a}^1 - \frac{1}{3}\boldsymbol{a}^2,\quad \boldsymbol{a}^3, \tag{12.19}$$

the sum of whose first three coefficients is equal to zero. For a plane specified by vector

$$\boldsymbol{n} = n_1\boldsymbol{a}^1 + n_2\boldsymbol{a}^2 + n_3\boldsymbol{a}^3, \tag{12.20}$$

the Bravais indices are

$$(n_1 \cdot \quad n_2 \cdot \quad -n_1 - n_2 \cdot \quad n_3). \tag{12.21}$$

On the contrary, a crystallographic plane with the Bravais indices

$$(p_1 p_2 p_3 p_4)$$

is specified by vector

$$\boldsymbol{n} = p_1 \boldsymbol{a}^1 + p_2 \boldsymbol{a}^2 + p_4 \boldsymbol{a}^3. \tag{12.22}$$

According to the definition, common in crystallography, the Bravais indices of crystallographic planes are integers without common factors, inversely proportional to the intercepts, expressed in terms of the units of measurement along the axis that are cut off by a given

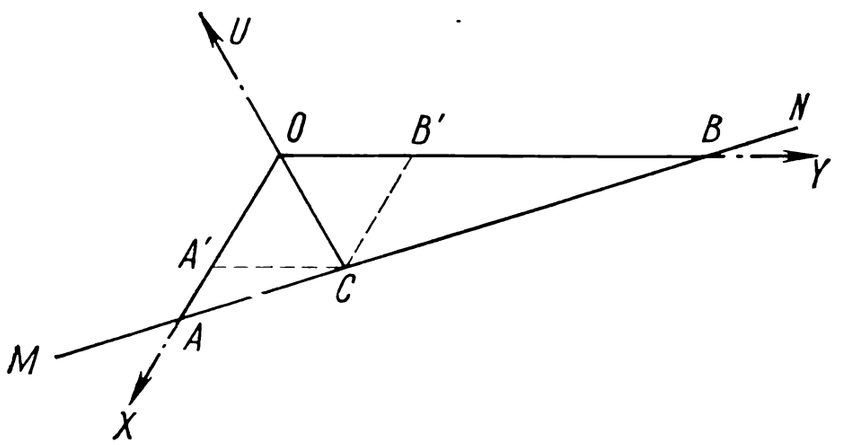


Fig. 12.3. To the proof of the theorem on the Bravais indices of a plane being proportional to the intercepts cut off by this plane on the XYZ and U axes

plane on the X, Y, U, Z axes respectively. Hence, it must be proved that the above formal definition of the Bravais indices and their common definition just given are equivalent.

As follows from the general theorem given at the beginning of this Section, the components n_1, n_2, n_3 of vector $\boldsymbol{n}$ are inversely proportional to the intercepts expressed in terms of units of measurement along the axis, that are cut off by a given plane on the X, Y and Z axes. But these components are equal to the first, second and fourth Bravais indices respectively. On the other hand, if a certain plane cuts intercepts d/n_1 and d/n_2 on axes X and Y respectively, the intercept on axis U is equal to $d/(-n_1 - n_2)$. Indeed let us consider Fig. 12.3. The line MN is the intersection line of the basal plane and a plane defined by vector $\boldsymbol{n}$. At points A, B, C, situated on this line, plane $\boldsymbol{n}$ intersects axes X, Y, U respectively. Apparently, $OA = d/n_1$ and $OB = d/n_2$. The intercept OC is cut off on axis U. Let us draw intercepts $CA' \parallel OB$ and $CB' \parallel OA$. Since $\angle AOC = \angle BOC = 60°$, it is evident that triangles OCA' and OCB' are equilateral. Now, using the similarity of triangles $A'CA$ and $B'CB$,

we derive the proportion $A'C : A'A = B'B : B'C$ or $\frac{OC}{d/n_1 - OC} = \frac{d/n_2 - OC}{OC}$ from which we find

$$-OC = -\frac{(d/n_1)(d/n_2)}{d/n_1 + d/n_2} = \frac{d}{-n_1 - n_2}, \tag{12.23}$$

which proves the case.

For the most widely used directions and planes Table 13.1 (see § 13) shows the Bravais and Miller indices related to the hexagonal system of coordinates (i.e. coefficients l^α or the expansion of the vector of crystallographic directions $\boldsymbol{l} = l^\alpha \boldsymbol{a}_\alpha$ in terms of the base vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ of the hexagonal lattice and the coefficients n_β of the expansion of the vector of the normal to the crystallographic plane $\boldsymbol{n} = n_\beta \boldsymbol{a}^\beta$ in terms of the base vectors $\boldsymbol{a}^1$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3$ of the reciprocal lattice).

Sec. 13. Transformation of Indices with a Change of the System of Coordinates

The transformation of coordinate systems is rarely dealt with in crystallography, because usually standard, fixed systems are used. There are cases, however, when a crystal can be described in two different standard systems of coordinates. For instance, crystals of the trigonal system are sometimes described not in the hexagonal, but in the rhombohedral system of coordinates. Besides, while in crystallography unit cells are mostly used, even if they are not primitive, in solid state physics primitive cells are preferred as a rule. In all such cases a change from one method of specifying to another is defined by a corresponding transformation of the vector basis of the lattice.

Let $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ be a certain vector basis of a crystal lattice. Let us agree to call it the "old basis" and consider, along with it, another lattice basis, $\boldsymbol{a}_{1'}$, $\boldsymbol{a}_{2'}$, $\boldsymbol{a}_{3'}$ which we shall agree to call the "new basis". Correspondingly, we shall call "old" and "new" the coordinate systems constructed on these bases. Knowing the components of any vector with respect to the old system of coordinates, we can calculate its components with respect to the new one; this operation, applied to all vectors present in the problem to be solved, is called the *transformation of the system of coordinates* or a change from an old system of coordinates to a new one.

Vectors of the new basis, just as any vectors, can be resolved into the old basis:

$$\boldsymbol{a}_{\beta'} = P^\alpha_{\beta'} \boldsymbol{a}_\alpha. \tag{13.1}$$

If the old base vectors define a unit cell, then all the coefficients $P^\alpha_{\beta'}$ are integers. If, however, a parallelepiped constructed on the

vectors of the old basis is not a unit one, the $P^{\alpha}_{\beta'}$ are not necessarily integers (but in any case they are rational).

Since the new base vectors are non-coplanar, the old base vectors can be resolved into the new basis:

$$a_{\alpha} = Q^{\gamma'}_{\alpha} a_{\gamma'}. \tag{13.2}$$

In order to find the relations connecting coefficients $Q^{\gamma'}_{\alpha}$ with coefficients $P^{\alpha}_{\beta'}$, we substitute expression (13.2) for a_{α} into equation (13.1)

$$a_{\beta'} = P^{\alpha}_{\beta'} Q^{\gamma'}_{\alpha} a_{\gamma'}.$$

Since base vectors are linearly independent, it follows from this equality that

$$P^{\alpha'}_{\beta'} Q^{\gamma'}_{\alpha} = \delta^{\gamma'}_{\beta'}. \tag{13.3}$$

But another way is also possible: equation (13.1) can be substituted for $a_{\beta'}$ into (13.2). This will result in an equality

$$a_{\gamma} = Q^{\beta'}_{\gamma} P^{\alpha}_{\beta'} a_{\alpha}.$$

Because of the linear independence of base vectors, there will follow from it

$$Q^{\beta'}_{\gamma} P^{\alpha}_{\beta'} = \delta^{\alpha}_{\gamma}. \tag{13.4}$$

The sets of coefficients $P^{\alpha}_{\beta'}$ and $Q^{\beta'}_{\alpha}$ form square matrices

$$P = \begin{Vmatrix} P^{1}_{1'} & P^{2}_{1'} & P^{3}_{1'} \\ P^{1}_{2'} & P^{2}_{2'} & P^{3}_{2'} \\ P^{1}_{3'} & P^{2}_{3'} & P^{3}_{3'} \end{Vmatrix}, \quad Q = \begin{Vmatrix} Q^{1'}_{1} & Q^{2'}_{1} & Q^{3'}_{1} \\ Q^{1'}_{2} & Q^{2'}_{2} & Q^{3'}_{2} \\ Q^{1'}_{3} & Q^{2'}_{3} & Q^{3'}_{3} \end{Vmatrix}.$$

Relations (13.3) and (13.4) can be written as matrix equalities

$$PQ = I, \quad QP = I. \tag{13.5}$$

Here

$$I = \begin{Vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{Vmatrix} \tag{13.6}$$

is the *unit matrix.*

If two matrices satisfy one of the relations (13.5), they will certainly satisfy the second one too. Such matrices are called *mutually reciprocal.* Knowing one of the mutually reciprocal matrices, let us say, P, it will not be difficult to find the elements of the other one. For this purpose it is necessary to calculate the determinant det P of matrix P and the signed minors $\Pi^{\beta'}_{\alpha}$ of its elements. The signed minor $\Pi^{\beta'}_{\alpha}$ of element $P^{\alpha}_{\beta'}$ of matrix P is equal to a determinant,

multiplied by $(-1)^{\alpha+\beta'}$, which will result from the determinant of matrix P, with eliminated column and line which contain element $P_{\beta'}$. Thereupon the elements $Q_\alpha^{\beta'}$ of matrix Q are calculated from equation

$$Q_\alpha^{\beta'} = \frac{1}{\det P} \Pi_\alpha^{\beta'}. \tag{13.7}$$

Let us introduce the Levy-Civita symbols

$$\delta_{\alpha\beta\gamma} = \begin{cases} 1 & \text{for} \quad \alpha\beta\gamma = 123,\ 231,\ 312, \\ -1 & \text{for} \quad \alpha\beta\gamma = 132,\ 213,\ 321, \\ 0 & \text{in other cases*} \end{cases} \tag{13.8}$$

and $\delta^{\alpha\beta\gamma}$ differing from the preceding only by having superscripts rather than subscripts. The relations (11.4) and (11.6) between the base vectors of the direct and reciprocal lattices are written, with the aid of the introduced symbols, in a compact and elegant form:

$$\begin{aligned} \boldsymbol{a}^\alpha &= \frac{1}{2v} \delta^{\alpha\beta\gamma} \boldsymbol{a}_\beta \times \boldsymbol{a}_\gamma, \\ \boldsymbol{a}_\alpha &= \frac{1}{2} v \delta_{\alpha\beta\gamma} \boldsymbol{a}^\beta \times \boldsymbol{a}^\gamma, \end{aligned} \tag{13.9}$$

as well as the formulas for the vector products of base vectors

$$\boldsymbol{a}_\alpha \times \boldsymbol{a}_\beta = v\delta_{\alpha\beta\gamma}\boldsymbol{a}^\gamma, \quad \boldsymbol{a}^\alpha \times \boldsymbol{a}^\beta = \frac{1}{v} \delta^{\alpha\beta\gamma} \boldsymbol{a}_\gamma. \tag{13.10}$$

The Levi-Civita symbols allow writing out very briefly the sequence of operations necessary for calculating the determinant of any (3×3) matrix S with elements $S_\varkappa^\alpha$

$$\det S = \delta_{\alpha\beta\gamma} S_1^\alpha S_2^\beta S_3^\gamma = \delta^{\alpha\beta\gamma} S_\alpha^1 S_\beta^2 S_\gamma^3. \tag{13.11}$$

Using these formulas we calculate the volume v' of a parallelepiped constructed on the new base vectors. Evidently, $v' = \boldsymbol{a}_{1'} \times \times (\boldsymbol{a}_{2'} \times \boldsymbol{a}_{3'})$. Having substituted the new base vectors by their expansions (13.1) we obtain

$$v' = P_{1'}^\alpha P_{2'}^\beta P_{3'}^\gamma \boldsymbol{a}_\alpha \cdot (\boldsymbol{a}_\beta \times \boldsymbol{a}_\gamma). \tag{13.12}$$

Using for the calculation of $\boldsymbol{a}_\beta \times \boldsymbol{a}_\gamma$ equation (13.10) and resorting to equation (11.2) we obtain

$$v' = v\delta_{\alpha\beta\gamma} P_{4'}^\alpha P_{2'}^\beta P_{3'}^\gamma. \tag{13.13}$$

* There is also another definition of the Levi-Civita symbol, a more compact one, but perhaps less lucid

$$\delta_{\alpha\beta\gamma} = \frac{1}{2} (\alpha - \beta)(\beta - \gamma)(\gamma - \alpha).$$

Comparing this expression with formula (13.11), we obtain the relation

$$v' = v \det P. \tag{13.14}$$

Thus, the determinant of matix P is equal to the ratio of the volume of a parallelepiped,constructed on new base vectors, to the volume of parallelepiped constructed on old base vectors. Apparently, $\det Q = v/v'$ (determinants of mutually reciprocal matrices are mutually reciprocal).

Now let us see how the reciprocal lattice basis will be transformed under the given transformation of the crystal lattice basis. Apparently, new covariant base vectors, $\boldsymbol{a}_{1'}$, $\boldsymbol{a}_{2'}$, $\boldsymbol{a}_{3'}$, will be reciprocated by new contravariant base vectors, $\boldsymbol{a}^{1'}$, $\boldsymbol{a}^{2'}$, $\boldsymbol{a}^{3'}$, defined by the relations

$$\boldsymbol{a}_{\alpha'} \cdot \boldsymbol{a}^{\gamma'} = \delta_{\alpha'}^{\gamma'}. \tag{13.15}$$

The new vectors are resolved in the old ones by means of matrix Q

$$\boldsymbol{a}^{\gamma'} = Q_{\eta}^{\gamma'} \boldsymbol{a}^{\eta}. \tag{13.16}$$

Indeed, under this transformation law $a_{\alpha'} \cdot a^{\gamma'} = P_{\alpha_1'}^{\beta} Q_{\eta}^{\gamma'} \boldsymbol{a}_{\beta} \cdot \boldsymbol{a}^{\eta}$ and then with the aid of (11.2) and (13.3) there is at once obtained the relation (13.15). It is evident that the old contravariant base vectors resolve into the new ones by means of matrix P:

$$\boldsymbol{a}^{\eta} = P_{\gamma'}^{\eta} \boldsymbol{a}^{\gamma'}. \tag{13.17}$$

Now it can be easily found out how the components of the lattice vectors, i.e. the Miller indices of crystallographic directions (edges) and crystallographic planes (faces) change under the transformation of their basis. We shall first consider the indices of crystallographic directions. For any vector $\boldsymbol{l}$ there will hold equality

$$\boldsymbol{l} = l^{\alpha} \boldsymbol{a}_{\alpha} = l^{\beta'} \boldsymbol{a}_{\beta'}. \tag{13.18}$$

For its realization it is necessary that

$$l^{\beta'} = Q_{\gamma}^{\beta'} l^{\gamma}. \tag{13.19}$$

Then, indeed $l^{\beta'} \boldsymbol{a}_{\beta'} = Q_{\gamma}^{\beta'} l^{\gamma} P_{\beta'}^{\alpha} \boldsymbol{a}_{\alpha}$, hence upon applying identity (13.4) equality (13.18) will be satisfied under this transformation law. And vice versa, the old components l^{α} are expressed in terms of the new ones with the aid of matrix P:

$$l^{\alpha} = P_{\beta'}^{\alpha} l^{\beta'}. \tag{13.20}$$

The transformation formulas for face indices are derived quite similarly:

$$n_{\beta'} = P_{\beta'}^{\alpha} n_{\alpha}, \tag{13.21}$$

$$n_{\alpha} = Q_{\alpha}^{\beta'} n_{\beta'}. \tag{13.22}$$

Now we shall tabulate all the results obtained in this section. The transition from the old quantities to the new ones we shall call "direct" transformation—it is characterized by formulas expressing new quantities as linear combinations of the old ones. The transition from the new quantities to the old ones we shall call "reverse" transformation. Thus we have

Quantities	Direct transformation	Reverse transformation
Base lattice vectors $\boldsymbol{a}_\alpha$	$\boldsymbol{a}_{\beta'} = P^{\alpha}_{\beta'}\boldsymbol{a}_\alpha$	$\boldsymbol{a}_\gamma = Q^{\beta'}_{\gamma}\boldsymbol{a}_{\beta'}$
Base reciprocal lattice vectors $\boldsymbol{a}^\alpha$	$\boldsymbol{a}^{\beta'} = Q^{\beta'}_{\alpha}\boldsymbol{a}^\alpha$	$\boldsymbol{a}^\gamma = P^{\gamma}_{\beta'}\boldsymbol{a}^{\beta'}$
Indices of planes (faces) n_α	$n_{\beta'} = P^{\alpha}_{\beta'}n_\alpha$	$n_\gamma = Q^{\beta'}_{\gamma}n_{\beta'}$
Indices of directions (edges) l^α	$l^{\beta'} = Q^{\beta'}_{\alpha}l^\alpha$	$l^\gamma = P^{\gamma}_{\beta'}l^{\beta'}$

The table shows that direct transformation of quantities with a subscript—of base lattice vectors $\boldsymbol{a}_\alpha$ and face indices n_α—is done by means of matrix P, while the reverse transformation is done by means of matrix Q. On the contrary, for quantities with a superscript—base vectors $\boldsymbol{a}^\alpha$ of reciprocal lattice and edge indices l^α—direct transformation depends on matrix Q, and reverse transformation on matrix P. The names of quantities are connected with this particular fact: the quantities with subscripts are called *covariant* (covariant base vectors $\boldsymbol{a}_\alpha$, covariant components n_α), because they are transformed in the same way as the principal vector basis, while the quantities with superscripts are called *contravariant* (contravariant base vectors $\boldsymbol{a}^\alpha$, contravariant components l^α), because they are transformed in the reverse manner, so to speak.

The names of the components of a metric tensor—"covariant" and "contravariant"—indicate the laws of transformation of these components under transition from one basis to another. The transformation laws follow directly from (11.8) and (11.11). If along with the old basis, $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, there is introduced a new basis, $\boldsymbol{a}_{1'}$, $\boldsymbol{a}_{2'}$, $\boldsymbol{a}_{3'}$, then according to (11.11) the transformation law of the covariant components of the metric tensor is expressed as

$$\begin{aligned} g_{\gamma'\eta'} &= P^{\alpha}_{\gamma'}P^{\beta}_{\eta'}g_{\alpha\beta}, \\ g_{\alpha\beta} &= Q^{\gamma'}_{\alpha}Q^{\eta'}_{\beta}g_{\gamma'\eta'}. \end{aligned} \tag{13.23}$$

Let us compare these formulas with (13.21), (13.22). Evidently, the covariant components of a metric tensor transform as the products of covariant components of two vectors. This property is used for the definition of the tensor. There are just nine quantities $f_{\alpha\beta}$ that

are called *covariant components of a second-rank tensor*, if they transform as the products of covariant components of two vectors. Moreover, 3^r of quantities $f_{\alpha_1 \ldots \alpha_r}$ are called *covariant components of an r-rank tensor*, if they are transformed as the products of covariant components of r vectors.

Prefix "co" can be replaced by "contra" in all the above explanations; corresponding definitions for the contravariant components of tensors will result. For example, from formulas (13.8), (13.16) and (13.17) there is derived the transformation law for the contravariant components of a metric tensor:

$$\begin{aligned} g^{\gamma'\eta'} &= Q_\alpha^{\gamma'} Q_\beta^{\eta'} g^{\alpha\beta}, \\ g^{\alpha\beta} &= P_{\gamma'}^{\alpha} P_{\eta'}^{\beta} g^{\gamma'\eta'}. \end{aligned} \tag{13.24}$$

Mixed tensor components are also possible; for instance, 9 quantities f_α^β are called *mixed* (to be more exact—they are called covariant—contravariant) *components of a second-rank tensor*, if they are transformed as the products of a covariant component of one vector by a contravariant component of another.

It has already been noted (see Sec. 12) that in principle any vector can be resolved both into a covariant and a contravariant basis; correspondingly, this vector will be specified by its contravariant or covariant components. A peculiar property of a metric tensor is that it determines the connection between both types of components and allows an easy change from one of them to the other.

For instance, let vector $\boldsymbol{l} = l^\alpha \boldsymbol{a}_\alpha$ be first specified by its contravariant components l^α. For finding its covariant components l_α it will suffice to resolve the covariant basic vectors $\boldsymbol{a}_\alpha$ into the contravariant ones: $\boldsymbol{a}_\alpha = g_{\alpha\beta}\boldsymbol{a}^\beta$. We now have $\boldsymbol{l} = l^\alpha g_{\alpha\beta}\boldsymbol{a}^\beta$. However, the coefficients of vector $\boldsymbol{l}$ in its expansion into the contravariant basis will be its covariant components l_β. Thus the contravariant components of the same vector are connected by the expression

$$l_\beta = l^\alpha g_{\alpha\beta}. \tag{13.25}$$

Equation

$$n^\beta = n_\alpha g^{\alpha\beta}, \tag{13.26}$$

might be derived similarly. The equation expresses the contravariant components of a vector in terms of its covariant ones. Equations (13.25) and (13.26) show that a metric tensor allows to write indices both as superscripts or subscripts. If, for example, we use a metric tensor for writing one of the indices of the contravariant components of the tensor as a subscript, or write one of the indices of its covariant components as a superscript, we shall obtain mixed (covariant—contravariant) components of the metric tensor:

$$g_\gamma^\alpha = g^{\alpha\beta} g_{\beta\gamma}.$$

Comparing this result with (11.13) we see that

$$g^{\alpha}_{\gamma} = \delta^{\alpha}_{\gamma}, \tag{13.27}$$

i.e. that the mixed components of the metric tensor coincide with Kronecker's symbols.

As an example of the transformation of coordinate systems we shall discuss the change from a rhombohedral system of coordinatel to a hexagonal one. Fig. 13.1 shows the projection of a rhombohedras lattice on a basal plane. Points within circles will be regarded as

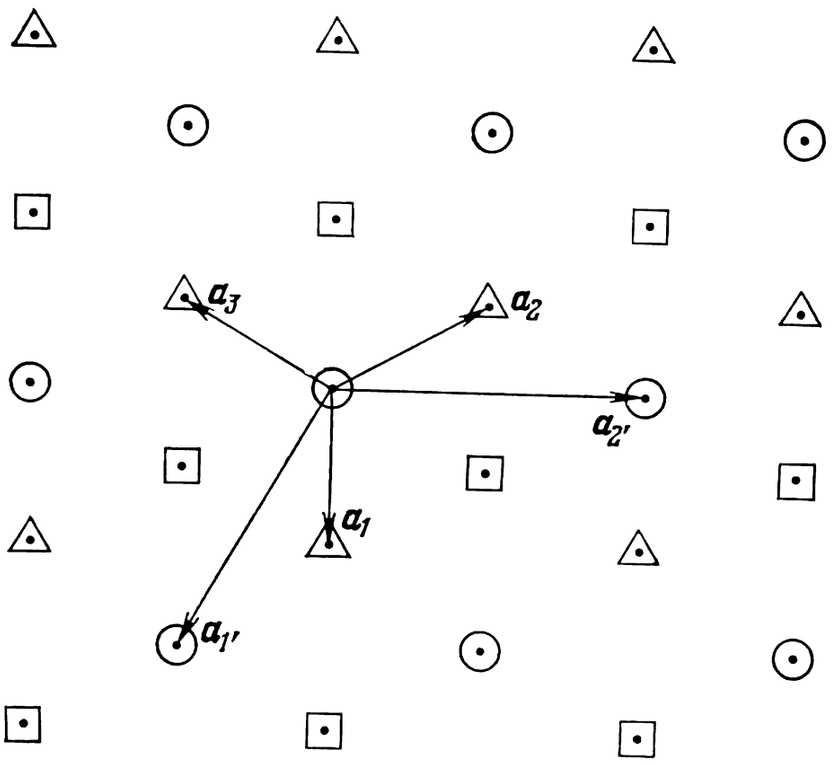


Fig. 13.1. Base vectors of the rhombohedral and hexagonal systems of coordinates in a rhombohedral lattice. Points within circles are in the plane of the paper, those within triangles are above, and those within squares are below, the plane of the paper

lying in the plane of the drawing. Directly over this plane are the points within triangles and directly below it are points within squares. The whole pattern is periodically repeated: thus, directly over the plane of points within triangles is another plane of points within squares, and, over the latter, still another plane of points within circles, etc.

The base vectors of the rhombohedral system of coordinates, $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, are directed from a point in the plane of the drawing to the nearest points on the plane directly above the plane of the paper.

Base vectors of the hexagonal system of coordinates, $\boldsymbol{a}_{1'}$ and $\boldsymbol{a}_{2'}$ lie in the plane of the paper. The third one, $\boldsymbol{a}_{3'}$ is not shown, since

it is normal to the plane of the paper; this vector is directed from the initial point to the nearest one that is exactly over it.

Fig. 13.1 shows the relations connecting the base vectors of both systems. Namely

$$\begin{aligned} a_{1'} &= a_1 - a_2, \\ a_{2'} &= a_2 - a_3, \\ a_{3'} &= a_1 + a_2 + a_3. \end{aligned} \tag{13.28}$$

Thus, matrix $\| P^{\alpha}_{\beta'} \|$ specifying the change from a rhombohedral to a hexagonal basis has the form

$$\begin{array}{c|ccc} & 1 & 2 & 3 \\ \hline 1' & 1 & -1 & 0 \\ 2' & 0 & 1 & -1 \\ 3' & 1 & 1 & 1 \end{array} \tag{13.29}$$

The determinant of this matrix det $P = 3$; this shows that the volume of a hexagonal cell is three times that of a rhombohedral one.

The matrix of a reverse transformation $\| Q^{\beta'}_{\gamma} \|$, according to (13.7) is

$$\begin{array}{c|ccc} & 1' & 2' & 3' \\ \hline 1 & 2/3 & 1/3 & 1/3 \\ 2 & -1/3 & 1/3 & 1/3 \\ 3 & -1/3 & -2/3 & 1/3 \end{array} \tag{13.30}$$

This means that the rhombohedral base vectors are resolved into the hexagonal ones in the following manner:

$$\begin{aligned} a_1 &= \frac{1}{3}(2a_{1'} + a_{2'} + a_{3'}), \\ a_2 &= \frac{1}{3}(-a_{1'} + a_{2'} + a_{3'}), \\ a_3 &= \frac{1}{3}(-a_{1'} - 2a_{2'} + a_{3'}). \end{aligned} \tag{13.31}$$

As has already been mentioned, the crystals of the trigonal and hexagonal systems are specified by means of Bravais indices which are connected with the hexagonal system of coordinates. Sometimes, however, crystals of the trigonal system are specified by Miller indices connected with the rhombohedral system of coordinates; precisely this method was used by the well-known crystallographer P. Groth in his classic handbook (Groth,1897),and even now it is occasionally used. It should be emphasized that Groth used Miller indices for specifying not only crystals with the rhombohedral Bra-

vais lattice, but also for those crystals of the trigonal system which had the hexagonal Bravais lattice. In the latter case the rhombohedral cell should be regarded as a unit one but not primitive, the hexagonal cell being primitive.

To understand the connection between the rhombohedral and hexagonal bases in this case too, we shall again look at Fig. 13.1. Let us imagine that points within triangles and squares are absent. The remaining points, within circles, form the hexagonal Bravais lattice; its unit cell is defined by vectors $\boldsymbol{a}_{1'}$, $\boldsymbol{a}_{2'}$, and $\boldsymbol{a}_{3'}$. Now let us note that vectors $3\boldsymbol{a}_1$, $3\boldsymbol{a}_2$, and $3\boldsymbol{a}_3$ are the vectors of the resulting hexagonal Bravais lattice. Apparently they are the ones that define the rhombohedral unit cell; its volume is three times that of the primitive hexagonal cell.

Let us derive the relations between the Bravais indices, connected with the hexagonal system of coordinates, and Miller indices, connected with the rhombohedral system. We begin with the symbols of directions (edges). Let the crystallographic direction be specified by Bravais indices $[r^1r^2r^3r^4]$. According to (12.18) the corresponding vector

$$\boldsymbol{l} = (r^1 - r^3)\,\boldsymbol{a}_{1'} + (r^2 - r^3)\,\boldsymbol{a}_{2'} + r^4\boldsymbol{a}_{3'}.$$

With the aid of (13.28) we resolve the base vectors $\boldsymbol{a}_{1'}$, $\boldsymbol{a}_{2'}$, $\boldsymbol{a}_{3'}$ of the hexagonal coordinate system in terms of the basis of the rhombohedral coordinate system:

$$\boldsymbol{l} = (r^1 - r^3)(\boldsymbol{a}_1 - \boldsymbol{a}_2) + (r^2 - r^3)(\boldsymbol{a}_2 - \boldsymbol{a}_3) + r^4(\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3).$$

Upon grouping of the similar terms we obtain

$$\boldsymbol{l} = (r^1 - r^3 + r^4)\,\boldsymbol{a}_1 + (r^2 - r^1 + r^4)\,\boldsymbol{a}_2 + (r^3 - r^2 + r^4)\,\boldsymbol{a}_3.$$

Thus, Miller indices of direction $[r^1r^2r^3r^4]$ are

$$[r^1 - r^3 + r^4.\quad r^2 - r^1 + r^4.\quad r^3 - r^2 + r^4]. \tag{13.32}$$

Any common factor should of course be cancelled out.

On the contrary, let a certain direction (edge) be specified in the rhombohedral system of coordinates by Miller indices $[l^1l^2l^3]$, i.e. let its corresponding vector be

$$\boldsymbol{l} = l^1\boldsymbol{a}_1 + l^2\boldsymbol{a}_2 + l^3\boldsymbol{a}_3.$$

With the aid of (13.4) we resolve vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, in the basis of the hexagonal system $\boldsymbol{a}_{1'}$, $\boldsymbol{a}_{2'}$, $\boldsymbol{a}_{3'}$. Grouping similar terms, we obtain

$$\boldsymbol{l} = \frac{2l^1 - l^2 - l^3}{3}\boldsymbol{a}_{1'} + \frac{l^1 - l^2 - 2l^3}{3}\boldsymbol{a}_{2'} + \frac{l^1 + l^2 + l^3}{3}\boldsymbol{a}_{3'}.$$

And now, with the aid of (12.8) we find the Bravais indices

$$[l^1 - l^2.\quad l^2 - l^3.\quad l^3 - l^1.\quad l^1 + l^2 + l^3]. \tag{13.33}$$

Let us now pass over to the symbols of crystallographic planes (faces). Let the Bravais indices of a certain crystallographic plane be $(p_1p_2p_3p_4)$. According to equations (12.22), this means that the vector of a normal to the plane is

$$\boldsymbol{n} = p_1\boldsymbol{a}^{1'} + p_2\boldsymbol{a}^{2'} + p_4\boldsymbol{a}^{3'}.$$

The covariant components of this vector in the hexagonal coordinate system are

$$n_{1'} = p_1, \quad n_{2'} = p_2, \quad n_{3'} = p_4.$$

The covariant components n_1, n_2, n_3 of the same vector in the rhombohedral system of coordinates will be found from (13.22), the elements of matrix Q having been given in (13.30). We obtain

$$n_1 = \frac{1}{3}(2n_{1'} + n_{2'} + n_{3'}) = \frac{1}{3}(p_1 - p_3 + p_4),$$

$$n_2 = \frac{1}{3}(-n_{1'} + n_{2'} + n_{3'}) = \frac{1}{3}(p_2 - p_1 + p_4),$$

$$n_3 = \frac{1}{3}(-n_{1'} - 2n_{2'} + n_{3'}) = \frac{1}{3}(p_3 - p_2 + p_4).$$

Thus Miller indices of the plane $(p_1p_2p_3p_4)$ are

$$(p_1 - p_3 + p_4. \quad p_2 - p_1 + p_4. \quad p_3 - p_2 + p_4). \tag{13.34}$$

And vice versa, if the crystallographic plane (face) is specified by Miller indices $(n_1n_2n_3)$ with respect to the rhombohedral coordinate system, the vector of a normal to the plane is

$$\boldsymbol{n} = n_1\boldsymbol{a}^1 + n_2\boldsymbol{a}^2 + n_3\boldsymbol{a}^3.$$

The covariant components of vector $\boldsymbol{n}$ relative to the hexagonal coordinate system are calculated with the aid of (13.21); the elements of matrix P having been given in (13.29). The $n_{\beta'}$ components are equal to

$$n_{1'} = n_1 - n_2,$$

$$n_{2'} = n_2 - n_3,$$

$$n_{3'} = n_1 + n_2 + n_3.$$

Now, from equation (12.22) we find the Bravais indices for this plane

$$(n_1 - n_2. \quad n_2 - n_3. \quad n_3 - n_1. \quad n_1 + n_2 + n_3). \tag{13.35}$$

Formulas (13.32) and (13.33) connecting the Bravais indices of crystallographic directions with their Miller indices in the rhombohedral system of coordinates coincide with expressions (13.34) and (13.35) that connect the Bravais and Miller indices of crystallographic planes. This was utilized in Table 13.1; the Bravais indices in the hexagonal system of coordinates (BH) and Miller indices in the

Table 13.1

Bravais Indices in Hexagonal Orientation, Miller Indices in Hexagonal Orientation for Planes and Directions and Miller Indices in Rhombohedral Orientation

Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)	Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)	Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)
0001	001	001	111	$\bar{2}111$	$\bar{2}11$	$\bar{3}01$	$\bar{2}41$	$\bar{2}3\bar{1}1$	$\bar{2}31$	$\bar{1}41$	$02\bar{1}$
$2\bar{1}\bar{1}0$	$2\bar{1}0$	100	$1\bar{1}0$	$1\bar{2}11$	$1\bar{2}1$	$0\bar{3}1$	$1\bar{2}4$	$\bar{1}\bar{2}31$	$\bar{1}\bar{2}1$	$\bar{4}\bar{5}1$	$\bar{1}02$
$\bar{1}2\bar{1}0$	$\bar{1}20$	010	$01\bar{1}$	$11\bar{2}1$	111	331	$41\bar{2}$	$\bar{3}121$	$\bar{3}11$	$\bar{5}\bar{1}1$	$\bar{4}52$
$\bar{1}\bar{1}20$	$\bar{1}\bar{1}0$	$\bar{1}\bar{1}0$	$\bar{1}01$	$\bar{1}012$	102	$\bar{2}\bar{1}2$	011	$2\bar{3}11$	$2\bar{3}1$	$1\bar{4}1$	$2\bar{4}5$
$\bar{2}110$	$\bar{2}10$	$\bar{1}00$	$\bar{1}10$	$1\bar{1}02$	$1\bar{1}2$	$1\bar{1}2$	101	$12\bar{3}1$	121	451	$52\bar{4}$
$1\bar{2}10$	$1\bar{2}0$	$0\bar{1}0$	$0\bar{1}1$	$01\bar{1}2$	012	122	110	$3\bar{2}\bar{1}1$	$3\bar{2}1$	$4\bar{1}1$	$5\bar{4}2$
$11\bar{2}0$	110	110	$10\bar{1}$	$10\bar{1}2$	102	212	411	$\bar{1}3\bar{2}1$	$\bar{1}31$	151	$25\bar{4}$
$10\bar{1}0$	100	210	$2\bar{1}\bar{1}$	$\bar{1}102$	$\bar{1}12$	$\bar{1}12$	141	$\bar{2}\bar{1}31$	$\bar{2}\bar{1}1$	$\bar{5}\bar{4}1$	$\bar{4}25$
$\bar{1}100$	$\bar{1}10$	$\bar{1}10$	$\bar{1}2\bar{1}$	$0\bar{1}12$	$0\bar{1}2$	$\bar{1}\bar{2}2$	114	$\bar{3}211$	$\bar{3}21$	$\bar{4}11$	$\bar{1}20$
$0\bar{1}10$	$0\bar{1}0$	$\bar{1}\bar{2}0$	$\bar{1}\bar{1}2$	$2\bar{1}\bar{1}2$	$2\bar{1}2$	302	$5\bar{1}2$	$1\bar{3}21$	$1\bar{3}1$	$\bar{1}\bar{5}1$	$0\bar{1}2$
$\bar{1}010$	$\bar{1}00$	$\bar{2}\bar{1}0$	$\bar{2}11$	$\bar{1}2\bar{1}2$	$\bar{1}22$	032	$25\bar{1}$	$21\bar{3}1$	211	541	$20\bar{1}$
$1\bar{1}00$	$1\bar{1}0$	$1\bar{1}0$	$1\bar{2}1$	$\bar{1}\bar{1}22$	$\bar{1}\bar{1}2$	$\bar{3}\bar{3}2$	$\bar{1}25$	$2\bar{1}\bar{1}3$	$2\bar{1}3$	101	201
$01\bar{1}0$	010	120	$11\bar{2}$	$\bar{2}112$	$\bar{2}12$	$\bar{3}02$	$\bar{1}52$	$\bar{1}2\bar{1}3$	$\bar{1}23$	011	120
$10\bar{1}1$	101	211	100	$1\bar{2}12$	$1\bar{2}2$	$0\bar{3}2$	$2\bar{1}5$	$\bar{1}\bar{1}23$	$\bar{1}\bar{1}3$	$\bar{1}\bar{1}1$	012
$\bar{1}101$	$\bar{1}11$	$\bar{1}11$	010	$11\bar{2}2$	112	332	$52\bar{1}$	$\bar{2}113$	$\bar{2}13$	$\bar{1}01$	021
$0\bar{1}11$	$0\bar{1}1$	$\bar{1}\bar{2}1$	001	$3\bar{1}\bar{2}0$	$3\bar{1}0$	510	$5\bar{4}\bar{1}$	$1\bar{2}13$	$1\bar{2}3$	$0\bar{1}1$	102
$\bar{1}011$	$\bar{1}01$	$\bar{2}\bar{1}1$	$\bar{1}22$	$\bar{2}3\bar{1}0$	$\bar{2}30$	$\bar{1}40$	$\bar{1}5\bar{4}$	$11\bar{2}3$	113	111	210
$1\bar{1}01$	$1\bar{1}1$	$1\bar{1}1$	$2\bar{1}2$	$\bar{1}\bar{2}30$	$\bar{1}\bar{2}0$	$\bar{4}\bar{5}0$	$\bar{4}\bar{1}5$	$30\bar{3}1$	301	631	$7\bar{2}\bar{2}$
$01\bar{1}1$	011	121	$22\bar{1}$	$\bar{3}120$	$\bar{3}10$	$\bar{5}\bar{1}0$	$\bar{5}41$	$\bar{3}301$	$\bar{3}31$	$\bar{3}31$	$\bar{2}7\bar{2}$
$\bar{2}021$	$\bar{2}01$	$\bar{4}\bar{2}1$	$\bar{1}11$	$2\bar{3}10$	$2\bar{3}0$	$1\bar{4}0$	$1\bar{5}4$	$0\bar{3}31$	$0\bar{3}1$	$\bar{3}\bar{6}1$	$\bar{2}\bar{2}7$
$2\bar{2}01$	$2\bar{2}1$	$2\bar{2}1$	$1\bar{1}1$	$12\bar{3}0$	120	450	$41\bar{5}$	$\bar{3}031$	$\bar{3}01$	$\bar{6}\bar{3}1$	$\bar{5}44$
$02\bar{2}1$	021	241	$11\bar{1}$	$3\bar{2}\bar{1}0$	$3\bar{2}0$	$4\bar{1}0$	$4\bar{5}1$	$3\bar{3}01$	$3\bar{3}1$	$3\bar{3}1$	$4\bar{5}4$
$20\bar{2}1$	201	421	$5\bar{1}\bar{1}$	$\bar{1}3\bar{2}0$	$\bar{1}30$	150	$14\bar{5}$	$03\bar{3}1$	031	361	$44\bar{5}$
$\bar{2}201$	$\bar{2}21$	$\bar{2}21$	$\bar{1}5\bar{1}$	$\bar{2}\bar{1}30$	$\bar{2}\bar{1}0$	$\bar{5}\bar{4}0$	$\bar{5}14$	$30\bar{3}2$	302	632	$8\bar{1}\bar{1}$
$0\bar{2}21$	$0\bar{2}1$	$\bar{2}\bar{4}1$	$\bar{1}\bar{1}5$	$\bar{3}210$	$\bar{3}20$	$\bar{4}10$	$\bar{4}5\bar{1}$	$\bar{3}302$	$\bar{3}32$	$\bar{3}32$	$\bar{1}8\bar{1}$
$2\bar{1}\bar{1}1$	$2\bar{1}1$	301	$4\bar{2}1$	$1\bar{3}20$	$1\bar{3}0$	$\bar{1}\bar{5}0$	$\bar{1}\bar{4}5$	$0\bar{3}32$	$0\bar{3}2$	$\bar{3}\bar{6}2$	$\bar{1}\bar{1}8$
$\bar{1}2\bar{1}1$	$\bar{1}21$	031	$14\bar{2}$	$21\bar{3}0$	210	540	$5\bar{1}\bar{4}$	$\bar{3}032$	$\bar{3}02$	$\bar{6}\bar{3}2$	$\bar{4}55$
$\bar{1}\bar{1}21$	$\bar{1}\bar{1}1$	$\bar{3}\bar{3}1$	$\bar{2}14$	$3\bar{1}\bar{2}1$	$3\bar{1}1$	511	$2\bar{1}0$	$3\bar{3}02$	$3\bar{3}2$	$3\bar{3}2$	$5\bar{4}5$

Table 13.1 (cont'd)

Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)	Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)	Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)
$03\bar{3}2$	032	362	$55\bar{4}$	$22\bar{4}3$	223	221	$31\bar{1}$	$21\bar{3}2$	212	542	$71\bar{2}$
$20\bar{2}3$	203	423	711	$10\bar{1}3$	103	213	522	$4\bar{1}\bar{3}0$	$4\bar{1}0$	720	$7\bar{5}\bar{2}$
$\bar{2}203$	$\bar{2}23$	$\bar{2}23$	171	$\bar{1}103$	$\bar{1}13$	$\bar{1}13$	252	$\bar{3}4\bar{1}0$	$\bar{3}40$	$\bar{2}50$	$\bar{2}7\bar{5}$
$0\bar{2}23$	$0\bar{2}3$	$\bar{2}\bar{4}3$	117	$0\bar{1}13$	$0\bar{1}3$	$\bar{1}\bar{2}3$	225	$\bar{1}\bar{3}40$	$\bar{1}30$	$\bar{5}70$	$\bar{5}\bar{2}7$
$\bar{2}023$	$\bar{2}03$	$\bar{4}\bar{2}3$	$\bar{1}55$	$\bar{1}013$	$\bar{1}03$	$\bar{2}\bar{1}3$	144	$\bar{4}130$	$\bar{4}10$	$\bar{7}\bar{2}0$	$\bar{7}52$
$2\bar{2}03$	$2\bar{2}3$	$2\bar{2}3$	$5\bar{1}5$	$1\bar{1}03$	$1\bar{1}3$	$1\bar{1}3$	414	$3\bar{4}10$	$3\bar{4}0$	$2\bar{5}0$	$2\bar{7}5$
$02\bar{2}3$	023	243	$55\bar{1}$	$01\bar{1}3$	013	123	441	$13\bar{4}0$	130	570	$52\bar{7}$
$40\bar{4}1$	401	841	$3\bar{1}\bar{1}$	$10\bar{1}4$	104	214	211	$4\bar{3}\bar{1}0$	$4\bar{3}0$	$5\bar{2}0$	$5\bar{7}2$
$\bar{4}401$	$\bar{4}41$	$\bar{4}41$	$\bar{1}3\bar{1}$	$\bar{1}104$	$\bar{1}14$	$\bar{1}14$	121	$\bar{1}4\bar{3}0$	$\bar{1}40$	270	$25\bar{7}$
$0\bar{4}41$	$0\bar{4}1$	$\bar{4}\bar{8}1$	$\bar{1}\bar{1}3$	$0\bar{1}14$	$0\bar{1}4$	$\bar{1}\bar{2}4$	112	$\bar{3}\bar{1}40$	$\bar{3}\bar{1}0$	$\bar{7}\bar{5}0$	$\bar{7}25$
$\bar{4}041$	$\bar{4}01$	$\bar{8}\bar{4}1$	$\bar{7}55$	$\bar{1}014$	$\bar{1}04$	$\bar{2}\bar{1}4$	255	$\bar{4}310$	$\bar{4}30$	$\bar{5}20$	$\bar{5}7\bar{2}$
$4\bar{4}01$	$4\bar{4}1$	$4\bar{4}1$	$5\bar{7}5$	$1\bar{1}04$	$1\bar{1}4$	$1\bar{1}4$	525	$1\bar{4}30$	$1\bar{4}0$	$\bar{2}\bar{7}0$	$\bar{2}\bar{5}7$
$04\bar{4}1$	041	481	$55\bar{7}$	$01\bar{1}4$	014	124	552	$31\bar{4}0$	310	750	$7\bar{2}\bar{5}$
$2\bar{1}\bar{1}4$	$2\bar{1}4$	304	714	$10\bar{1}5$	105	215	744	$5\bar{2}\bar{3}0$	$5\bar{2}0$	810	$8\bar{7}\bar{1}$
$\bar{1}2\bar{1}4$	$\bar{1}24$	034	471	$\bar{1}105$	$\bar{1}15$	$\bar{1}15$	474	$\bar{3}5\bar{2}0$	$\bar{3}50$	$\bar{1}70$	$\bar{1}8\bar{7}$
$\bar{1}\bar{1}24$	$\bar{1}\bar{1}4$	$\bar{3}\bar{3}4$	147	$0\bar{1}15$	$0\bar{1}5$	$\bar{1}\bar{2}5$	447	$\bar{2}\bar{3}50$	$\bar{2}30$	$\bar{7}\bar{8}0$	$\bar{7}\bar{1}8$
$\bar{2}114$	$\bar{2}14$	$\bar{3}04$	174	$\bar{1}015$	$\bar{1}05$	$\bar{2}\bar{1}5$	122	$\bar{5}230$	$\bar{5}20$	$\bar{8}\bar{1}0$	$\bar{8}71$
$1\bar{2}14$	$1\bar{2}4$	$0\bar{3}4$	417	$1\bar{1}05$	$1\bar{1}5$	$1\bar{1}5$	212	$3\bar{5}20$	$3\bar{5}0$	$1\bar{7}0$	$1\bar{8}7$
$11\bar{2}4$	114	334	741	$01\bar{1}5$	015	125	221	$23\bar{5}0$	230	780	$71\bar{8}$
$4\bar{2}\bar{2}1$	$4\bar{2}1$	601	$7\bar{5}1$	$3\bar{1}\bar{2}2$	$3\bar{1}2$	512	$7\bar{2}1$	$5\bar{3}\bar{2}0$	$5\bar{3}0$	$7\bar{1}0$	$7\bar{8}1$
$\bar{2}4\bar{2}1$	$\bar{2}41$	061	$17\bar{5}$	$\bar{2}3\bar{1}2$	$\bar{2}32$	$\bar{1}42$	$17\bar{2}$	$2\bar{5}30$	$\bar{2}50$	180	$17\bar{8}$
$22\bar{4}1$	$\bar{2}\bar{2}1$	$\bar{6}\bar{6}1$	$\bar{5}17$	$\bar{1}232$	$\bar{1}22$	$\bar{4}\bar{5}2$	$\bar{2}17$	$\bar{3}\bar{2}\bar{5}0$	$\bar{3}\bar{2}0$	$\bar{8}\bar{7}0$	$\bar{8}17$
$\bar{4}221$	$\bar{4}21$	$\bar{6}01$	$\bar{5}71$	$\bar{3}122$	$\bar{3}12$	$\bar{5}\bar{1}2$	$\bar{1}21$	$\bar{5}320$	$\bar{5}30$	$\bar{7}10$	$\bar{7}8\bar{1}$
$2\bar{4}21$	$2\bar{4}1$	$0\bar{6}1$	$1\bar{5}7$	$2\bar{3}12$	$2\bar{3}2$	$1\bar{4}2$	$1\bar{1}2$	$2\bar{5}30$	$2\bar{5}0$	$\bar{1}\bar{8}0$	$\bar{1}\bar{7}8$
$22\bar{4}1$	221	661	$71\bar{5}$	$12\bar{3}2$	122	$45\bar{2}$	$21\bar{1}$	$32\bar{5}0$	320	870	$8\bar{1}\bar{7}$
$4\bar{2}\bar{2}3$	$4\bar{2}3$	201	$3\bar{1}1$	$3\bar{2}\bar{1}2$	$3\bar{2}2$	$4\bar{1}2$	$2\bar{1}1$	$4\bar{1}31$	$4\bar{1}1$	721	$8\bar{4}\bar{1}$
$\bar{2}4\bar{2}3$	$\bar{2}43$	021	$13\bar{1}$	$\bar{1}3\bar{2}2$	$\bar{1}32$	152	$12\bar{1}$	$\bar{3}4\bar{1}1$	$\bar{3}41$	$\bar{2}51$	$\bar{1}8\bar{4}$
$\bar{2}\bar{2}43$	$\bar{2}\bar{2}3$	$\bar{2}\bar{2}1$	$\bar{1}13$	$\bar{2}132$	$\bar{2}\bar{1}2$	$\bar{5}\bar{4}2$	$\bar{1}12$	$\bar{1}\bar{3}41$	$\bar{1}\bar{3}1$	$\bar{5}\bar{7}1$	$\bar{4}\bar{1}8$
$\bar{4}223$	$\bar{4}23$	$\bar{2}01$	$\bar{1}31$	$\bar{3}212$	$\bar{3}22$	$\bar{4}\bar{1}2$	$\bar{2}71$	$\bar{4}131$	$\bar{4}11$	$\bar{7}\bar{2}1$	$\bar{2}21$
$2\bar{4}23$	$2\bar{4}3$	$0\bar{2}1$	$1\bar{1}3$	$1\bar{3}22$	$1\bar{3}2$	$\bar{1}\bar{5}2$	$1\bar{2}7$	$3\bar{4}11$	$3\bar{4}1$	$2\bar{5}1$	$1\bar{2}2$

Table 13.1 (cont'd)

Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)	Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)	Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)
$13\bar{4}1$	131	571	$21\bar{2}$	$03\bar{3}4$	034	364	$77\bar{2}$	$51\bar{6}1$	511	11.7.1	$4\bar{1}\bar{2}$
$4\bar{3}\bar{1}1$	$4\bar{3}1$	$5\bar{2}1$	$2\bar{2}1$	$40\bar{4}3$	403	843	$11.\bar{1}.\bar{1}$	$2\bar{1}\bar{1}6$	$2\bar{1}6$	306	312
$\bar{1}4\bar{3}1$	$\bar{1}41$	271	$12\bar{2}$	$\bar{4}403$	$\bar{4}43$	$\bar{4}43$	$\bar{1}.11.\bar{1}$	$\bar{1}2\bar{1}6$	$\bar{1}26$	036	231
$\bar{3}\bar{1}41$	$\bar{3}\bar{1}1$	$\bar{7}\bar{5}1$	$\bar{2}12$	$0\bar{4}43$	$0\bar{4}3$	$\bar{4}\bar{8}3$	$\bar{1}.\bar{1}.11$	$\bar{1}\bar{1}26$	$\bar{1}\bar{1}6$	$\bar{3}\bar{3}6$	123
$\bar{4}311$	$\bar{4}31$	$\bar{5}21$	$\bar{4}8\bar{1}$	$\bar{4}043$	$\bar{4}03$	$\bar{8}\bar{4}3$	$\bar{5}77$	$\bar{2}116$	$\bar{2}16$	$\bar{3}06$	132
$1\bar{4}31$	$1\bar{4}1$	$\bar{2}\bar{7}1$	$\bar{1}\bar{4}8$	$4\bar{4}03$	$4\bar{4}3$	$4\bar{4}3$	$7\bar{5}7$	$1\bar{2}16$	$1\bar{2}6$	$0\bar{3}6$	213
$31\bar{4}1$	311	751	$8\bar{1}\bar{4}$	$04\bar{4}3$	043	483	$77\bar{5}$	$11\bar{2}6$	116	336	321
$4\bar{1}\bar{3}2$	$4\bar{1}2$	722	$3\bar{1}0$	$4\bar{2}\bar{2}5$	$4\bar{2}5$	605	$11.\bar{1}.5$	$5\bar{1}\bar{4}0$	$5\bar{1}0$	$\bar{1}20$	$3\bar{2}\bar{1}$
$\bar{3}4\bar{1}2$	$\bar{3}42$	$\bar{2}52$	$03\bar{1}$	$\bar{2}4\bar{2}5$	$\bar{2}45$	065	$5.11.\bar{1}$	$\bar{4}51\bar{0}$	$\bar{4}50$	$\bar{2}\bar{3}0$	$\bar{1}3\bar{2}$
$\bar{1}\bar{3}42$	$\bar{1}\bar{3}2$	$\bar{5}\bar{7}2$	$\bar{1}03$	$\bar{2}\bar{2}45$	$\bar{2}\bar{2}5$	$\bar{6}\bar{6}5$	$\bar{1}.5.11$	$\bar{1}\bar{4}50$	$\bar{1}\bar{4}0$	$3\bar{1}0$	$\bar{2}\bar{1}3$
$\bar{4}132$	$\bar{4}12$	$\bar{7}\bar{2}2$	$\bar{5}74$	$\bar{4}225$	$\bar{4}25$	$\bar{6}05$	$\bar{1}.11.5$	$\bar{5}140$	$\bar{5}10$	$\bar{3}10$	$\bar{3}21$
$3\bar{4}12$	$3\bar{4}2$	$2\bar{5}2$	$4\bar{5}7$	$2\bar{4}25$	$2\bar{4}5$	$0\bar{6}5$	$5.\bar{1}.11$	$451\bar{0}$	$4\bar{5}0$	$1\bar{2}0$	$1\bar{3}2$
$13\bar{4}2$	132	572	$74\bar{5}$	$22\bar{4}5$	225	665	$11.5.\bar{1}$	$14\bar{5}0$	140	230	$21\bar{3}$
$4\bar{3}\bar{1}2$	$4\bar{3}2$	$5\bar{2}2$	$7\bar{5}4$	$50\bar{5}2$	502	10.5.2	$4\bar{1}\bar{1}$	$5\bar{4}\bar{1}0$	$5\bar{4}0$	$2\bar{1}0$	$2\bar{3}1$
$\bar{1}4\bar{3}2$	$\bar{1}42$	272	$47\bar{5}$	$\bar{5}502$	$\bar{5}52$	$\bar{5}52$	$\bar{1}4\bar{1}$	$\bar{1}5\bar{4}0$	$\bar{1}50$	130	$12\bar{3}$
$\bar{3}\bar{1}42$	$\bar{3}\bar{1}2$	$\bar{7}\bar{5}2$	$\bar{5}47$	$0\bar{5}52$	$0\bar{5}2$	$\bar{5}.\bar{1}\bar{0}.2$	$\bar{1}\bar{1}4$	$4\bar{1}50$	$\bar{4}\bar{1}0$	$\bar{3}\bar{2}0$	$\bar{3}12$
$\bar{4}312$	$\bar{4}32$	$\bar{5}22$	$\bar{1}30$	$\bar{5}052$	$\bar{5}02$	$\bar{1}\bar{0}.\bar{5}.2$	$\bar{8}77$	$\bar{5}410$	$\bar{5}40$	$\bar{2}10$	$\bar{2}3\bar{1}$
$1\bar{4}32$	$1\bar{4}2$	$\bar{2}\bar{7}2$	$0\bar{1}3$	$5\bar{5}02$	$5\bar{5}2$	$5\bar{5}2$	$7\bar{8}7$	$1\bar{5}40$	$1\bar{5}0$	$\bar{1}\bar{3}0$	$\bar{1}\bar{2}3$
$31\bar{4}2$	312	752	$30\bar{1}$	$05\bar{5}2$	052	5.10.2	$77\bar{8}$	$41\bar{5}0$	410	320	$3\bar{1}\bar{2}$
$20\bar{2}5$	205	425	311	$6\bar{1}51$	$6\bar{1}1$	11.4.1	$4\bar{2}\bar{1}$	$5\bar{2}\bar{3}2$	$5\bar{2}2$	812	$10.\bar{5}.1$
$\bar{2}205$	$\bar{2}25$	$\bar{2}25$	131	$\bar{5}6\bar{1}1$	$\bar{5}61$	$\bar{4}71$	$\bar{1}4\bar{2}$	$\bar{3}5\bar{2}2$	$\bar{3}52$	$\bar{1}72$	$1.10.\bar{5}$
$0\bar{2}25$	$0\bar{2}5$	$\bar{2}\bar{4}5$	113	$\bar{1}\bar{5}61$	$\bar{1}51$	$\bar{7}.\bar{1}\bar{1}.1$	$\bar{2}\bar{1}4$	$\bar{2}\bar{3}52$	$\bar{2}\bar{3}5$	$\bar{7}\bar{8}2$	$\bar{5}.1.10$
$\bar{2}025$	$\bar{2}05$	$\bar{4}\bar{2}5$	177	$\bar{6}151$	$\bar{6}11$	$\bar{1}\bar{1}.\bar{4}.1$	$\bar{1}\bar{0}.8.5$	$\bar{5}232$	$\bar{5}22$	$\bar{8}\bar{1}2$	$\bar{2}31$
$2\bar{2}05$	$2\bar{2}5$	$2\bar{2}5$	717	$5\bar{6}11$	$5\bar{6}1$	$4\bar{7}1$	$5.\bar{1}\bar{0}.8$	$3\bar{5}22$	$3\bar{5}2$	$1\bar{7}2$	$1\bar{2}3$
$02\bar{2}5$	025	245	771	$15\bar{6}1$	151	7.11.1	$8.5.\bar{1}\bar{0}$	$23\bar{5}2$	232	782	$31\bar{2}$
$30\bar{3}4$	304	634	10.1.1	$6\bar{5}\bar{1}1$	$6\bar{5}1$	$7\bar{4}1$	$8.\bar{1}\bar{0}.5$	$5\bar{3}\bar{2}2$	$5\bar{3}2$	$7\bar{1}2$	$3\bar{2}1$
$\bar{3}304$	$\bar{3}34$	$\bar{3}34$	1.10.1	$\bar{1}6\bar{5}1$	$\bar{1}61$	4.11.1	$5.8.\bar{1}\bar{0}$	$\bar{2}5\bar{3}2$	$\bar{2}52$	182	$13\bar{2}$
$0\bar{3}34$	$0\bar{3}4$	$\bar{3}\bar{6}4$	1.1.10	$\bar{5}161$	$\bar{5}11$	$\bar{1}\bar{1}.\bar{7}.1$	$\bar{1}\bar{0}.5.8$	$\bar{3}\bar{2}52$	$\bar{3}\bar{2}2$	$\bar{8}\bar{7}2$	$\bar{2}13$
$\bar{3}034$	$\bar{3}04$	$\bar{6}\bar{3}4$	$\bar{2}77$	$\bar{6}511$	$\bar{6}51$	$\bar{7}41$	$\bar{2}4\bar{1}$	$\bar{5}322$	$\bar{5}32$	$\bar{7}12$	$\bar{5}.10.1$
$3\bar{3}04$	$3\bar{3}4$	$3\bar{3}4$	$7\bar{2}7$	$1\bar{6}51$	$1\bar{6}1$	$\bar{4}.\bar{1}\bar{1}.1$	$\bar{1}\bar{2}4$	$2\bar{5}32$	$2\bar{5}2$	$\bar{1}\bar{8}2$	$1.\bar{5}.10$

Table 13.1 (cont'd)

Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)	Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)	Bravais hexagonal (BH)	Miller indices planes (MIP)	Miller indices directions (MID)	Miller rhombohedral (MR)
$32\bar{5}2$	322	872	$10.1.\bar{5}$	$3\bar{4}14$	$3\bar{4}4$	$2\bar{5}4$	$2\bar{1}3$	$\bar{3}144$	$\bar{3}\bar{1}4$	$\bar{7}\bar{5}4$	$\bar{1}23$
$41\bar{3}4$	$4\bar{1}4$	724	$11.\bar{1}.2$	$13\bar{4}4$	134	574	$32\bar{1}$	$\bar{4}314$	$\bar{4}34$	$\bar{5}24$	$\bar{1}.11.2$
$\bar{3}4\bar{1}4$	$\bar{3}44$	$\bar{2}54$	$2.11.\bar{1}$	$43\bar{1}4$	$4\bar{3}4$	$5\bar{2}4$	$3\bar{1}2$	$1\bar{4}34$	$1\bar{4}4$	$\bar{2}\bar{7}4$	$2.\bar{1}.11$
$\bar{1}\bar{3}44$	$\bar{1}\bar{3}4$	$\bar{5}\bar{7}4$	$\bar{1}.2.11$	$\bar{1}4\bar{3}4$	$\bar{1}44$	274	$23\bar{1}$	$31\bar{4}4$	314	754	$11.2.\bar{1}$
$\bar{4}134$	414	$\bar{7}\bar{2}4$	$\bar{1}32$								

Note. The Table gives the symbols of planes and directions projected onto the upper hemisphere of projections; therefore in the first three columns the last index is non-negative, while in the last column the sum of indices is non-negative. If a plane or direction is projected onto the lower hemisphere of projections, the symbol of the opposite plane of the reverse direction should be considered — all its indices will be opposite ones. Thus, there is no symbol BH $31\bar{4}\bar{4}$ in the Table, but having found the symbol BH $\bar{3}\bar{1}44$, we can see that to the BH $31\bar{4}\bar{4}$ there correspond MIP $31\bar{4}$, MID $75\bar{4}$ and MR $\bar{1}\bar{2}3$.

rhombohedral set (MR) are equally related to planes (faces) and directions (edges). The table also gives Miller indices for planes and directions referred to the hexagonal system of coordinates. The former (MIP) are the coefficients n_α of the expansion of the vector of a normal to the crystallographic plane $\boldsymbol{n} = n_\alpha \boldsymbol{a}^\alpha$ in terms of the principal vectors of a reciprocal lattice, $\boldsymbol{a}^\alpha$; the latter (MID) are the l^α coefficients of the expansion of the vector of crystallographic direction $\boldsymbol{l} = l^\alpha \boldsymbol{a}_\alpha$ in terms of the basic vectors of a crystal lattice $\boldsymbol{a}_\alpha$. In other words, MIP are the covariant components of vector $\boldsymbol{n}$ and MID are the contravariant components of vector $\boldsymbol{l}$.

Sec. 14. Symmetrically Equivalent Sets of Planes and Directions. Simple Crystal Forms

Symmetrical transformations inherent in crystal point groups symmetrically repeat any plane and any direction of a crystal in space. Let us take, for instance, plane (100) for a crystal of the $m3m$ class. Repeating it by all symmetric transformations we obtain planes $(\bar{1}00)$, (010), $(0\bar{1}0)$, (001) and $(00\bar{1})$. The totality of six symmetrically equivalent planes is denoted by symbol {100}: the braces show that all interchanges can be made in indices that would correspond to the symmetric transformations of the given symmetry class.

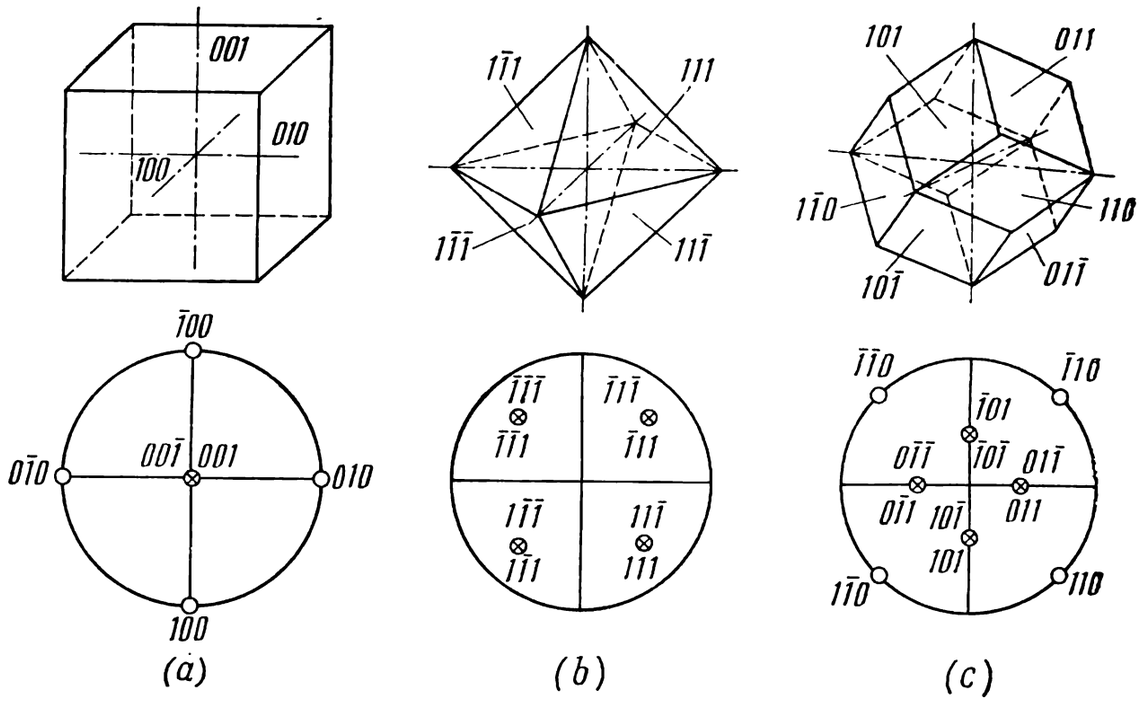


Fig. 14.1. Three simple forms of the $m3m$ class: cube (a); octahedron (b); and rhombic dodecahedron (c), and the set of their symmetry elements (for simplifying the drawing the face indices are given without brackets)

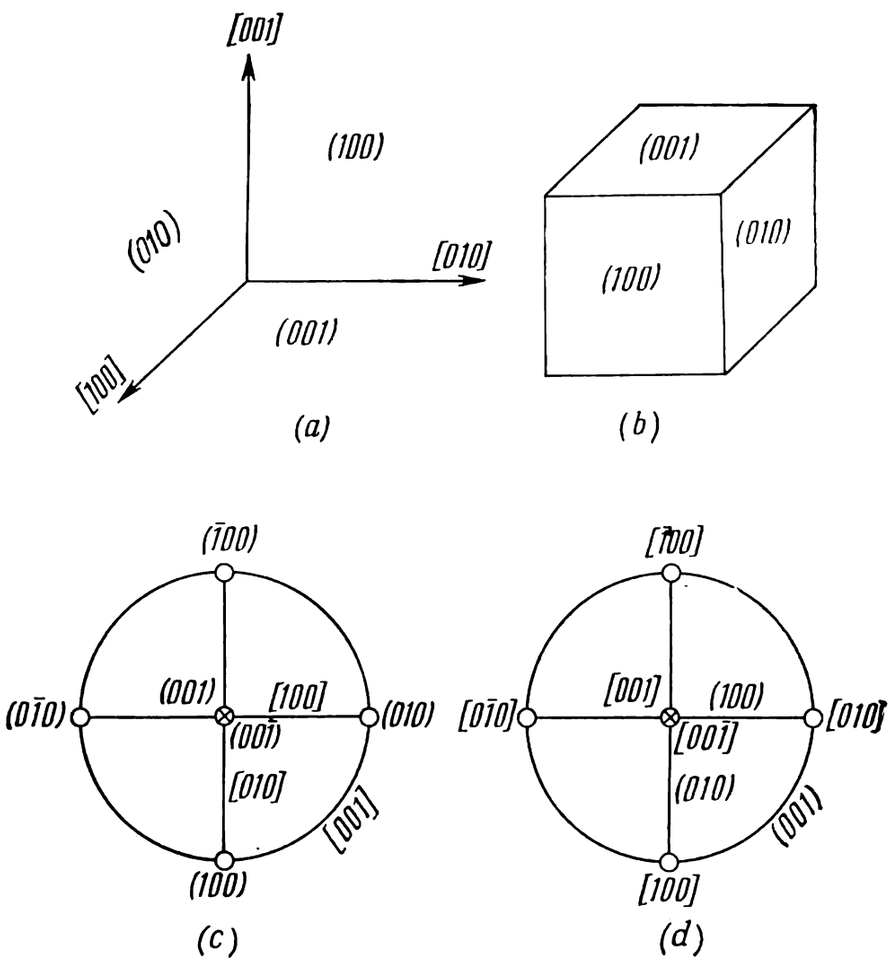


Fig. 14.2. Three ways of representing symmetrically equivalent planes and directions: a combination of planes and directions intersecting at a single point (a); faces and edges of a simple form (b); stereographic (c); and gnomostereographic (d) projections

If index (100) denotes a plane net of the structure, symbol {100} means the totality of the three coordinate planes in a lattice and the whole totality of planes parallel to them. But if symbol (100) means a crystal face, then {100} would mean a simple crystal form, i.e. the totality of symmetrically equivalent faces of a polyhedron. In the $m3m$ class it is the cube (Fig. 14.1).

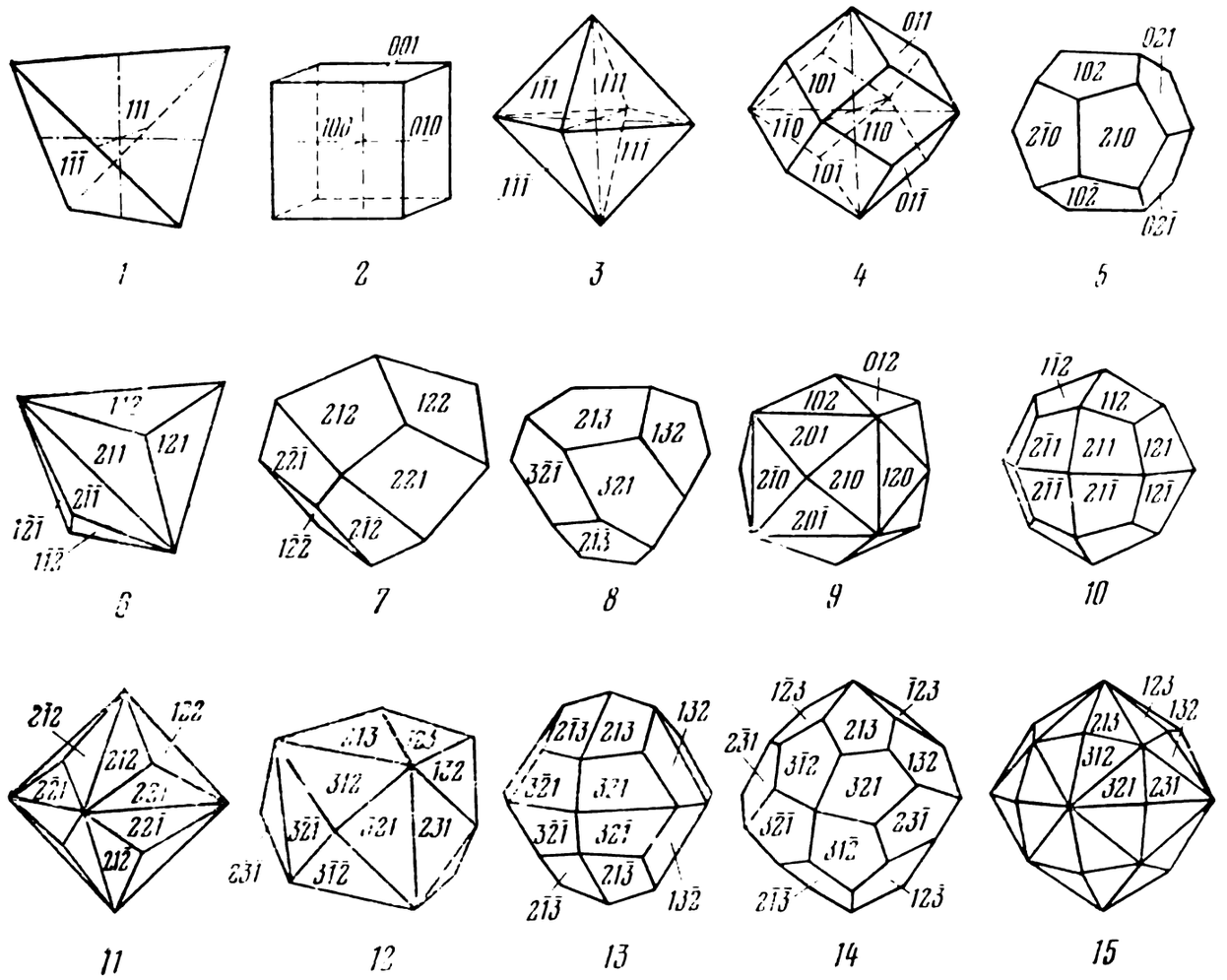


Fig. 14.3. Simple forms of the higher category: *1*—tetrahedron; *2*—cube; *3*—octahedron; *4*—rhombic dodecahedron; *5*—pentagondodecahedron; *6*—trigontritetrahedron; *7*—tetragontritetrahedron; *8*—pentagontritetrahedron; *9*—pyramidal cube; *10*—tetragontrioctahedron; *11*—trigontrioctahedron; *12*—hexatetrahedron; *13*—didodecahedron; *14*—pentagontrioctahedron; *15*—hexaoctahedron (face indices are given without brackets to simplify the drawing)

A simple form is a polyhedron all faces of which can be made to coincide with each other with the aid of transformations of symmetry inherent in the given crystal.

Applying the same symmetrical transformations of the $m3m$ class to the [100] direction in the lattice we shall obtain [$\bar{1}$00], [010], [0$\bar{1}$0], [001], and [00$\bar{1}$], i.e. positive and negative directions of the coordinate axes. We denote the set of symmetrically equivalent directions by symbol ⟨100⟩. If [100] is the edge of a polyhedron,

then ⟨100⟩ is the ensemble of symmetrically equivalent edges, or edge simple form. In the *m*3*m* class these are the cube edges. If [100] is a row in the lattice, ⟨100⟩ is the symbol of the coordinate axes and of all directions parallel to them (Fig. 14.2).

In our instance the initial plane (100) is in a special position, i.e. at the emergence of a 4-fold axis which is an element of the higher symmetry in the *m*3*m* class. Let us have the initial face in other special positions: at the emergence of a 3-fold axis we shall have eight symmetrically equivalent faces of an octahedron {111} and at the

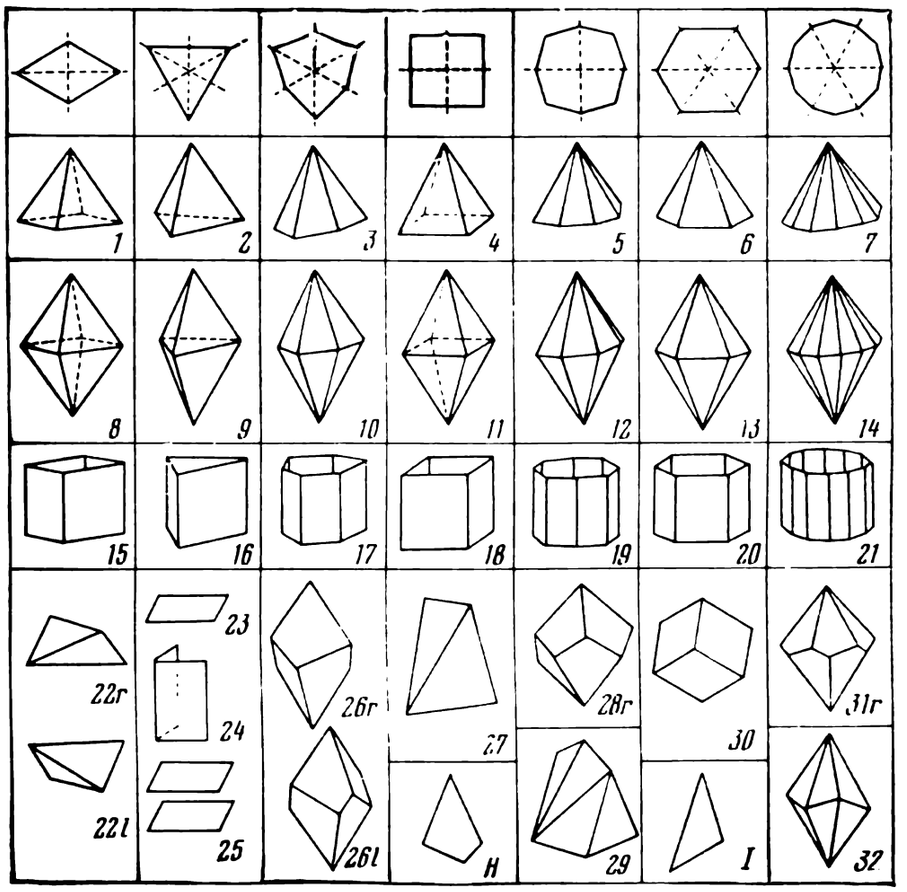


Fig. 14.4. Simple forms of the lower and intermediate categories. Upper row—sections of simple forms: rhomb, trigon, ditrigon, tetragon, ditetragon, hexagon, dihexagon; *1-7*—pyramids; *8-14*—dipyramids; *15-21*—prisms; *1*, *8*, *15*—rhombic; *2*, *9*, *16*—trigonal; *3*, *10*, *17*—ditrigonal; *4*, *11*, *18*—tetragonal; *5*, *12*, *19*—ditetragonal; *6*, *13*, *20*—hexagonal; *7*, *14*, *21*—dihexagonal; 22*r*, 22*l* — right- and left-hand rhombic tetrahedrons; *23*—monohedron; *24*—dihedron; *25*—pinacoid; *26r* and *l*—right-and left-handed trigonal trapezohedrons; *27*—tetragonal tetrahedron; *28r*—right-hand tetragonal trapezohedron; *H*—form of a trapezohedron face; *29*—tetragonal scalenohedron; *30*—rhombohedron; *31r*—right-hand hexagonal trapezohedron; *32*—ditrigonal scalenohedron; *I*—form of a scalenohedron face

emergence of a 2-fold axis twelve faces of a rhombic dodecahedron {110}. Taking the initial face in the most general position, so that it does not fit any of the symmetry elements and is inclined to all the three coordinate axes at different angles, we shall obtain the highest simple form of the *m*3*m* class—a hexoctahedron (Fig. 14.3).

To each symmetry class there correspond one general and several special simple forms. The $m3m$ class belongs to the highest symmetry. It is also rich in simple forms. The number of faces of its simple forms are respectively: 48 $\{hkl\}$; 24 $\{hhl\}$, $\{hk0\}$; 12 $\{110\}$; 8 $\{111\}$; 6 $\{100\}$. In the least symmetric of the cubic system classes, class 23, the number of simple form faces is respectively: 12 $\{hkl\}$, $\{hhl\}$; $\{hk0\}$, $\{110\}$; 6 $\{110\}$; 4 $\{111\}$.

Classes of a lower symmetry have a lesser variety of simple forms. To class m of the monoclinic system there corresponds a general form, dihedron $\{hkl\}$, i.e. two parallel faces, and a particular form consisting of a single face—monohedron $\{100\}$ or $\{010\}$, while class 1 has only one simple form, a monohedron (Fig. 14.4).

Simple forms can be space-enclosing, such as a cube, and an octahedron, and open, such as prisms, pyramids, pinacoids. Real forms of crystal growth are usually combinations of several simple forms. Open forms can occur only in combinations. The combinations can be most varied and their number is unlimited, but of simple forms there are only 47 (Boldyrev, 1936). They are all given in Tables 14.1 and 14.2 and in Figs. 14.3 and 14.4.

Table 14.1

Possible Simple Forms and Their Symbols in Cubic Crystals
(Digits in italics mean the number of simple forms in Fig. 14.3)

Symbol	Class				
	23	$m3$	432	$\bar{4}3m$	$m3m$
hkl	*8*	*13*	*14*	*12*	*15*
hhl $(h > l)$	*7*	*11*		*7*	*11*
hhl $(h < l)$	*6*	*9*		*6*	*9*
$hk0$	*5*		*12*		
111	*1*	*3*		*1*	*3*
110	*4*				
100	*2*				

The meaning of a simple form symbol depends on the class of symmetry to which it is related and on the choice of the crystallographic system of coordinates. For example, in the $m3m$ class in symbol $\{100\}$ permutations produce six planes of a cube, while in the class $2/m$ in the same symbol $\{100\}$ only one permutation is possible: (100) and $(\bar{1}00)$, i.e. only two planes are produced.

Sign-value of a simple form is the name given to the number of its faces,i.e. the number of symmetrically equivalent planes. The sign-value of a general simple form of a given point group is equal to the order, or multiplicity, of the point group, i.e. to the total number of equivalent points which can be obtained from a point by all the symmetry transformations inherent in the point group. Of the 32 point groups the *m*3*m* group has the highest order,its multiplicity being 48. The order of a group is determined by the number of equivalent points in gnomostereographic projection, or, in other words, by the number of faces of the general simple form.The particular simple forms correspond to the subgroups of a given point group. In each of the seven or six crystallographic systems there is one group of the higher order, the so-called *holohedry* (holohedric symmetry class). To this class there corresponds a general simple form with the greatest number of faces. The other point groups of a given crystallographic system are the following: *merohedral*—the subgroups of the holohedral group; *hemihedral*—the subgroups of index 2; *tetartohedral*—of index 4; *ogdohedral*—of index 8. They can be arranged in a series in which each subsequent group is a subgroup of the preceding group and is derived from the holohedral one by contraction of the sign-value, i.e. by decreasing the number of faces of the general simple form. Hemihedry corresponds to cutting the number of faces in two, tetartohedry—in four, ogdohedry—in 8. For instance,in the cubic system the *m*3*m* group is holohedral, *m*3, 432, $\bar{4}3m$ are hemihedral, 23 is tetartohedral. The number of faces is correspondingly 1/2, 1/4 or 1/8 of the number of faces of the holohedral general form.

In the intermediate and lower categories the decrease in the number of faces of a general simple form occurs as though the polyhedron is divided into the lower and the upper halves; for instance, in losing the transverse symmetry plane a dipyramid contracts to a pyramid, which in this case will be a hemimorphous form, the principal axis becoming now polar.

If we regard the hexagonal and trigonal systems as a single hexagonal one, class 3 will be an ogdohedry of the hexagonal system; the number of faces of the general simple form of class 3, a trigonal pyramid, is 8 times less than the number of faces of the general simple form of the holohedral class 6/*mmm* of a dihexagonal dipyramid. If the hexagonal and trigonal systems are taken separately, then class 3 will be the tetartohedry of class $\bar{3}\,m$, and class 6, the tetartohedry of class 6/*mmm*.

Interrelations of point groups and subgroups are shown in the diagram of Fig. 14.5. Thick dashed lines connect the groups of one system. Thus, the highest group of the rhombic system *mmm* includes two subgroups 222 and *mm*2. Since the *mmm* group has three two-fold axes, each of which can be the only two-fold axis in the *mm*2

Table 14.2

Possible Simple Forms and Their Symbols in Crystals of the Intermediate and Lower Categories

(Digits in italics mean the number of simple forms in Fig. 14.4)

Triclinic system: class 1-*23*, class $\bar{1}$-*25*

Monoclinic system

Symbol	Class		
	2	*m*	*2/m*
hkl	*24*		*15*
h0l	*25*	*23*	*25*
010	*23*	*25*	

Rhombic system

Symbol	Class		
	222	*mm2*	*mmm*
hkl	*22*	*1*	*8*
hk0	*15*		
0kl	*15*	*24*	*15*
100, 010	*25*		
001	*25*	*23*	

Trigonal system

Symbol	Class				
	3	$\bar{3}$	32	3*m*	$\bar{3}$*m*
hkil			*26*	*10*	*32*
$h0\bar{h}l$	*2*	*30*	*30*	*2*	*30*
$hh\overline{2h}l$			*9*	*6*	*13*
*hki*0			*17*		*21*
$10\bar{1}0$	*16*	*20*	*20*	*16*	*20*
$11\bar{2}0$			*16*	*20*	
0001	*23*	*25*		*23*	*25*

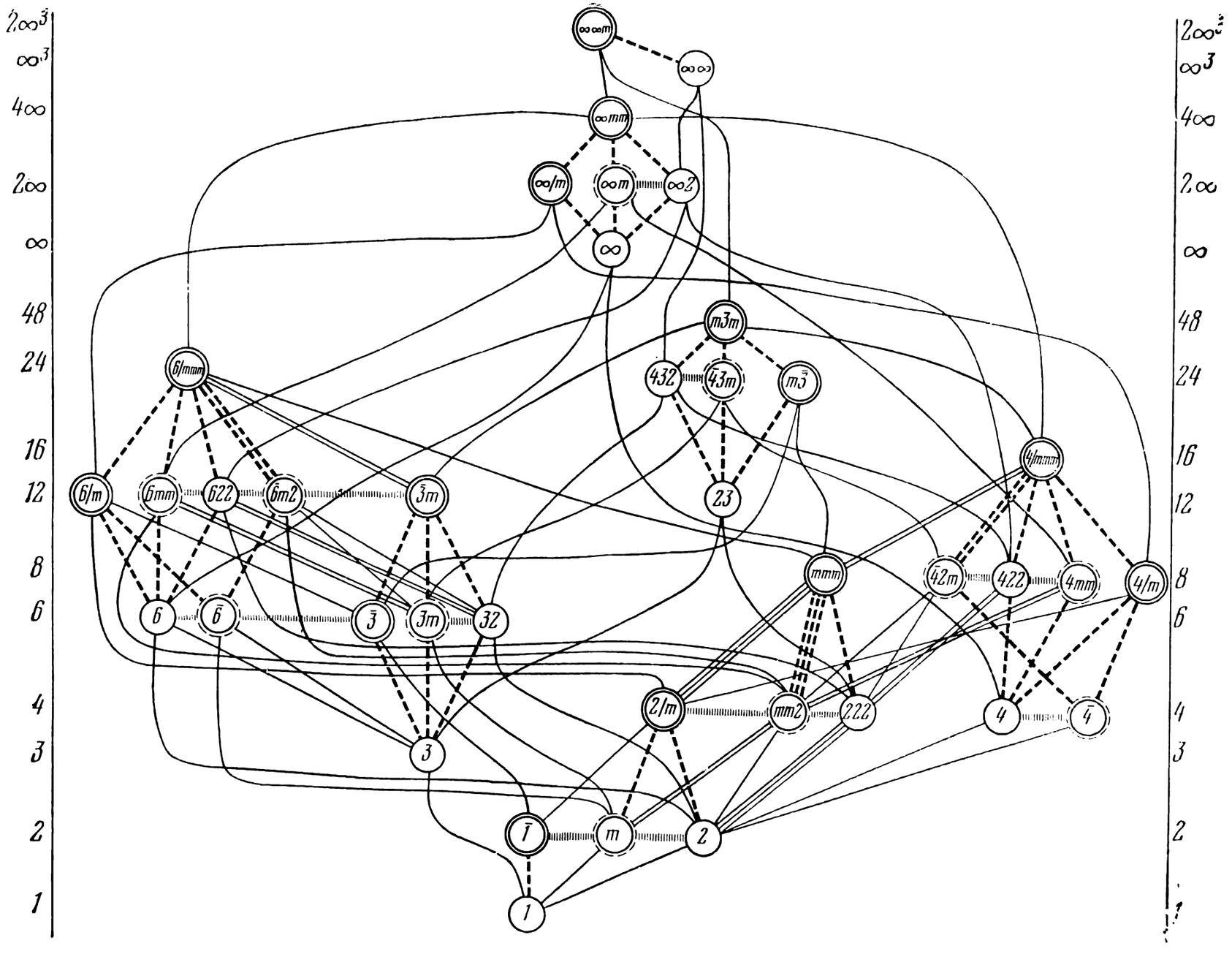
Table 14.2 (cont'd)

Hexagonal system

Symbol	Class						
	6	$\bar{6}$	6/m	622	6mm	$\bar{6}m2$	6/mmm
hkil	6	9	13	31	7	10	13
$h0\bar{h}l$				13		9	
$hh\overline{2h}l$						13	
*hki*0	20	16	20	21		17	21
$10\bar{1}0$				20			
$11\bar{2}0$				20		16	20
0001	23	25		23		25	

Tetragonal system

Symbol	Class						
	4	$\bar{4}$	4/m	422	4mm	$\bar{4}2m$	4/mmm
hkl	4	27	12	28	5	29	12
hhl				11	4	27	11
*h*0*l*						11	
*hk*0	11			19			
110				18			
100							
001	23	25			23	25	


2∞³
∞³
4∞
2∞
∞
48
24
16
12
8
6
4
3
2
1
∞∞m
∞∞
∞mm
∞/m
∞m
∞3
∞
m3m
6/mmm
432
4̄3m
m3̄
4/mmm
6/m
6mm
622
6m2
3̄m
23
mmm
4̄2m
422
4mm
4/m
6
6̄
3̄
3m
32
2/m
mm2
222
4
4̄
3
1̄
m
2
1

group, the *mmm* group contains three subgroups: $mm2_x$, $mm2_y$, $mm2_z$, in Fig. 14.5 it is shown by a triple dashed line.

A subgroup of the *mmm* group is also the $2/m$ group which does not belong to the rhombic system but is the highest group of the monoclinic system; the connection between them is shown by a thin line. There are three thin lines corresponding to the three possible directions of the two-fold axis: 2_x, 2_y, 2_z.

The $2/m$ group, in its turn, includes two groups of the monoclinic system, 2 and *m* which can be arranged in series in the following manner: $2/m \supset 2 \supset 1$, $2/m \supset m \supset 1$. Moreover, the $2/m \supset \bar{1} \supset 1$ series shows that groups of the triclinic system are also subgroups of the $2/m$ group.

Special attention should be paid to the ties between the groups of the cubic and trigonal systems: $m3m \supset 3\bar{m}$, $432 \subset 32$, $\bar{4}3m \supset 3m$, $m3 \supset \bar{3}$ and $23 \supset 3$. At standard orientations of crystals they are not sufficiently lucid and become quite evident when the direction

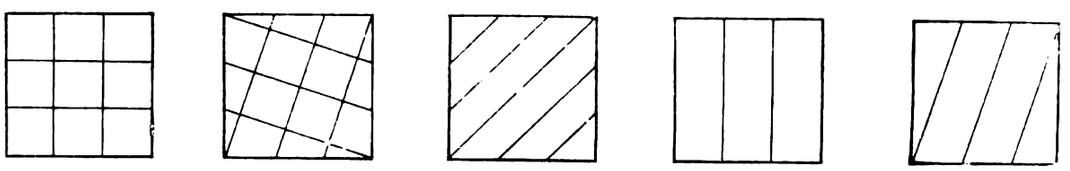


Fig. 14.6. Symmetry of the faces of five crystallographically different cubes (according to A. V. Shubnikov)

[111] of a cubic crystal is aimed at axis *Z*, and the direction $[\bar{1}\bar{1}0]$ at axis *X*. Horizontal dashed lines connect the isomorphous groups.

The multiplicity of each subgroup is shown on the right and left sides of Fig. 14.5. The number of faces of the general and special simple forms for each class of symmetry can be found at once from Fig. 14.5.

To each symmetry class there corresponds only one general and several special forms. A special form can be found, in its turn, in several symmetry classes. For instance, a cube can exist in all classes of the cubic system. If polyhedrons are considered not only as geometric bodies, but as material bodies with definite physical properties, in particular with different symmetry of faces, then it can be seen that geometrically congruent bodies can be crystallographically different if they differ by symmetry elements or by the arrangement of these elements with respect to a face.

In each of the five classes of the cubic system a cube is obtained as a special form, if the initial face is located in the centre of the projection. But the arrangement of the available symmetry elements with respect to the cube face will be different, and consequently the symmetry of the face itself will also be different. Five crystallographically different cubes can be shown by different hatching or shading

of their faces (Fig. 14.6) (Shubnikov, Flint, Bokyi, 1940). It can be seen from these hatchings that five congruent geometric solids can have entirely different symmetry of their faces and different symmetry of their physical properties. Moreover, in classes 23 and 432 cubes can be enantiomorphous (Fig. 14.7).

Crystallographic differences of geometrically congruent forms are quite real. They can be revealed by the growth irregularities, from the striation of the natural faces of crystals or from etch pits, i.e. small pits, predominantly with crystallographic faces, formed on the crystal faces by some active solvent. Etch pits are formed in

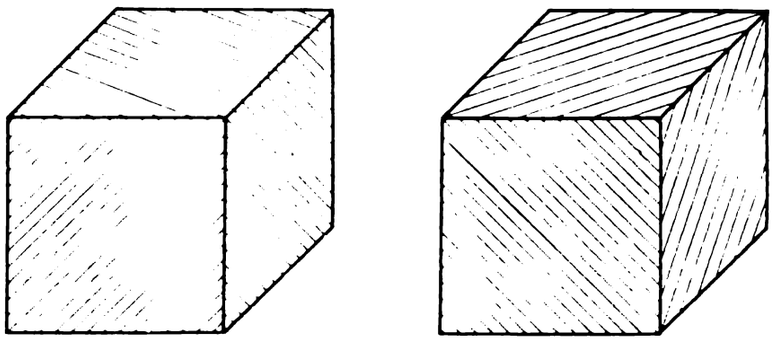


Fig. 14.7. Right- and left-hand cubes of class **23**

places where some imperfection of the crystal structure, mainly dislocations, reach the surface of the crystal. The true symmetry of a face can be recognized with the aid of the shape of etch figures. Geometrically similar but physically different planes and directions are characterized by the difference in physical properties.

G. B. Bokyi (1940) showed that there are 146 crystallographically different simple forms of crystals, and if the right- and left-handed forms are taken account of separately, the total number will be 193. I. I. Shafranovsky (1968) derived 1403 structural varieties of those same simple forms, differing in this case by infinite symmetry, i.e. by symmetry elements of space groups.

Besides its simple polyhedral form, a crystal can also be specified by its vertex and edge forms. A simple vertex form is the totality of the vertices of a crystal obtained from each other with the aid of all its symmetry operations, an edge form is a similar totality of edges.

A simple three-dimensional bundle of edges is the totality of edges connected by the symmetry elements of the given class and translated parallel to themselves into a single initial point. Thus, in the $m3m$ class symbol ⟨100⟩ means the totality of cube edges, as well as the set of 4-fold axes; a bundle of the directions of 3-fold axes has symbol ⟨111⟩. The stereogram of a simple edge form coincides with the gnomostereographic projection of a simple face form.

In an isotropic optically inactive media any direction is non-polar, non-axial, not singular, it has the highest symmetry and is spec-

ified by the symmetry group ∞/mm, i.e. by the symmetry of an infinite fixed cylinder. The symmetry of any direction can be found in a crystal by considering, according to the Curie principle, the superposition of the symmetry elements of the crystal and the cylinder oriented in the direction whose symmetry is sought (Zheludev, 1971). This sought for symmetry of direction is defined as the general highest subgroup of both groups satisfying the specified orientation of the crystal and cylinder.

Polar directions are subordinate to group ∞m, i.e. to the symmetry of a fixed circular cone. Group ∞m includes 10 polar classes: 1, 2, 3, 4, 6, m, $mm2$, $3m$, $4mm$, $6mm$. These classes have singular polar directions. Non-singular polar directions can be found in all acentral classes, including the polar-neutral ones, 222, 23, $\bar{6}$, $\bar{6}m2$, 622, $\bar{4}$, $\bar{4}2m$, 422, $\bar{4}3m$, 432.

Axial directions are specified by groups subject to the symmetry group ∞/m: 1, 2, 3, 4, 6, m, $2/m$, $\bar{6}$, $4/m$, $6m$, $\bar{1}$, $\bar{4}$, $\bar{3}$. Such directions are possible in all crystals.

Non-polar directions are available in 30 classes, being absent only from classes 1 and 3. In class 1 all directions are singular, polar. In class 3 the 3-fold axis is singular polar, all other directions are simple polar.

Sec. 15. Some Problems of Geometric Crystallography

The connection between Miller indices for faces and edges and vectors perpendicular to faces or parallel to edges allows to reduce many crystallographic problems to purely geometric ones. Let us consider some of these problems.

Problem 1. **Can direction $[l^1l^2l^3]$ be an edge of face $(n_1n_2n_3)$?** For the given direction $\boldsymbol{l}$ to be an edge of a face, it should be parallel to this face and consequently perpendicular to the normal $\boldsymbol{n}$ to the face. The condition of the perpendicularity of two vectors is the vanishing of their scalar product

$$\boldsymbol{l}\cdot\boldsymbol{n} = 0. \tag{15.1}$$

Since

$$\begin{aligned} \boldsymbol{l} &= l^1\boldsymbol{a}_1 + l^2\boldsymbol{a}_2 + l^3\boldsymbol{a}_3, \\ \boldsymbol{n} &= n_1\boldsymbol{a}^1 + n_2\boldsymbol{a}^2 + n_3\boldsymbol{a}^3, \end{aligned} \tag{15.2}$$

this condition is rewritten as

$$(l^1\boldsymbol{a}_1 + l^2\boldsymbol{a}_2 + l^3\boldsymbol{a}_3)\cdot(n_1\boldsymbol{a}^1 + n_2\boldsymbol{a}^2 + n_3\boldsymbol{a}^3) = 0. \tag{15.3}$$

Perform scalar multiplication termwise taking into account that

$$\boldsymbol{a}_\alpha\cdot\boldsymbol{a}^\beta = \delta_\alpha^\beta \tag{15.4}$$

Only three of the nine terms will not turn identically to zero, so that we finally obtain $l^1 n_1 + l^2 n_2 + l^3 n_3 = 0$, or, remembering the Einstein summation symbol,

$$l^\alpha n_\alpha = 0. \tag{15.5}$$

Direction $[l^1 l^2 l^3]$ can be the edge of face $(n_1 n_2 n_3)$ if and only if it satisfies condition (15.5). This expression can be derived much quicker by using Einstein's symbol from the very beginning. Instead of expansions (15.2) we write

$$\boldsymbol{l} = l^\alpha \boldsymbol{a}_\alpha, \quad \boldsymbol{n} = n_\beta \boldsymbol{a}^\beta, \tag{15.6}$$

and instead of condition (15.3)

$$l^\alpha \boldsymbol{a}_\alpha \cdot n_\beta \boldsymbol{a}^\beta = 0. \tag{15.7}$$

Now we use equality (15.4) and, instead of (15.7), we can write

$$l^\alpha n_\beta \delta_\alpha^\beta = 0. \tag{15.8}$$

Let us calculate the expression $n_\beta \delta_\alpha^\beta$. By definition

$$n_\beta \delta_\alpha^\beta = n_1 \delta_\alpha^1 + n_2 \delta_\alpha^2 + n_3 \delta_\alpha^3. \tag{15.9}$$

In this sum only one term differs from zero, which one depends on the value of index α. If, for instance, $\alpha = 1$, then $\delta_\alpha^1 = \delta_1^1 = 1$, while $\delta_\alpha^2 = \delta_1^2 = 0$ and $\delta_\alpha^3 = \delta_1^3 = 0$. In this case only the first term of sum (15.9), $n_\beta \delta_1^\beta = n_1$, differs from zero (and is equal to n_1). If $\alpha = 2$, the only non-zero term in the sum will be the second one, since $\delta_2^1 = \delta_2^3 = 0$, and $\delta_2^2 = 1$, hence $n_\beta \delta_2^\beta = n_2$. We can similarly see that $n_\beta \delta_3^\beta = n_3$. Obviously these three equalities can be replaced with one

$$n_\beta \delta_\alpha^\beta = n_\alpha \tag{15.10}$$

where index α can have any of the three possible values. In the same way it could be shown that

$$l^\alpha \delta_\alpha^\beta = l^\beta. \tag{15.11}$$

The obtained formulas (15.10) and (15.11) allow the formulation of the following general rule: when any quantity multiplied by the Kronecker's symbol is summed up the result will not change if the symbol is not written at all, and the summation index is replaced by the free index of the Kronecker's symbol.

Using either (15.10) or (15.11) for simplifying (15.8) we obtain the solution of the problem. Substituting (15.10) into (15.8) we get

$$l^\alpha n_\alpha = 0. \tag{15.12}$$

This is a short form of the solution (15.5) obtained above. (15.11) can be substituted into (15.8). Then we shall have $l^\beta n_\beta = 0$. The left-hand side is the same sum; the change of the summation indices is of no importance, as has already been mentioned.

Graphically the problem is easily solved with the aid of stereographic projection: direction $[l^1 l^2 l^3]$ can be the edge of face $(n_1 n_2 n_3)$ if the point representing direction isinside the great circle representing the plane. The solution can also be easily obtained with the aid of gnomostereographic projection: the great circle representing the direction $[l^1 l^2 l^3]$ should pass through the point representing plane $(n_1 n_2 n_3)$.

Problem 2. **The Miller symbol is to be found for the edge at which faces $(n_1 n_2 n_3)$ and $(m_1 m_2 m_3)$ intersect.** The edge sought for lies on both faces. Therefore vector $\boldsymbol{l}$ that specifies it is perpendicular to the normals $\boldsymbol{n}$ and $\boldsymbol{m}$ to both faces. Let us remember that this is just the property of the vector product of two vectors: it is a vector perpendicular to each of the factors of the product. We shall use the vector product multiplied by the volume of crystallographic cell v (it is evident that if a vector is multiplied by a positive number, its direction will not change):

$$\boldsymbol{l} = v\boldsymbol{n} \times \boldsymbol{m}. \tag{15.13}$$

The sequence of the factors is not essential in this case, because the direction of the edge will be anyway determined up to its sign. Let us calculate this vector product, taking into account that

$$\boldsymbol{n} = n_1 \boldsymbol{a}^1 + n_2 \boldsymbol{a}^2 + n_3 \boldsymbol{a}^3, \quad \boldsymbol{m} = m_1 \boldsymbol{a}^1 + m_2 \boldsymbol{a}^2 + m_3 \boldsymbol{a}^3.$$

Substitute this into (15.13)

$$\boldsymbol{l} = v\,(n_1 \boldsymbol{a}^1 + n_2 \boldsymbol{a}^2 + n_3 \boldsymbol{a}^3) \times (m_1 \boldsymbol{a}^1 + m_2 \boldsymbol{a}^2 + m_3 \boldsymbol{a}^3).$$

Let us perform a term-by-term vector multiplication, taking into account that the vector product of each vector by itself is equal to zero and that in permuting the factors the vector product changes its sign. We obtain

$$\boldsymbol{l} = v\,[(n_2 m_3 - n_3 m_2)\,\boldsymbol{a}^2 \times \boldsymbol{a}^3 + (n_3 m_1 - n_1 m_3)\,\boldsymbol{a}^3 \times \boldsymbol{a}^1 + \\ + (n_1 m_2 - n_2 m_1)\,\boldsymbol{a}^1 \times \boldsymbol{a}^2].$$

As has been calculated in Sec. 11 vector products of basic vectors of a reciprocal lattice multiplied by the volume of a crystallographic cell define base vectors of the direct lattice (this is why the factor v is introduced!). With the aid of (11.6) we find

$$l = (n_2 m_3 - n_3 m_2)\,\boldsymbol{a}_1 + (n_3 m_1 - n_1 m_3)\,\boldsymbol{a}_2 + (n_1 m_2 - n_2 m_1)\,\boldsymbol{a}_3. \tag{15.14}$$

Since numbers n_α and m_α are integers, the coefficients of base vectors are also integers; apparently they are the sought for Miller indices

of edge $[l^1 l^2 l^3]$:

$$l^1 = n_2 m_3 - n_3 m_2,\ l^2 = n_3 m_1 - n_1 m_3,\quad l^3 = n_1 m_2 - n_2 m_1. \tag{15.15}$$

Using the Levi-Civita symbols (see Sec.13) we write (15.13) as

$$\boldsymbol{l} = v n_\alpha \boldsymbol{a}^\alpha \times m_\beta \boldsymbol{a}^\beta \tag{15.16}$$

and with the aid of formulas (13.10) we obtain $\boldsymbol{l} = \delta^{\alpha\beta\gamma} n_\alpha m_\beta \boldsymbol{a}_\gamma$, whence follows

$$l^\gamma = \delta^{\gamma\alpha\beta} n_\alpha m_\beta. \tag{15.17}$$

This formula can be very easily used if we notice that having established one index, we leave only two possibilities for the values of the remaining two indices. Thus, if $\gamma = 1$, then only $\delta^{123} = 1$ and $\delta^{132} = -1$ differ from zero. Therefore

$$l^1 = \delta^{1\alpha\beta} n_\alpha m_\beta = \delta^{123} n_2 m_3 + \delta^{132} n_3 m_2 = n_2 m_3 - n_3 m_2,$$

which coincides with the first of the expressions (15.15).

A simple mnemonics is often used for solving Problem 2: Miller indices of faces $(n_1 n_2 n_3)$ and $(m_1 m_2 m_3)$ are written in two lines and cross-multiplication is performed

$$\begin{array}{c|cccc|c} n_1 & n_2 & n_3 & n_1 & n_2 & n_3 \\ & \times & \times & \times & & \\ m_1 & m_2 & m_3 & m_1 & m_2 & m_3 \end{array}$$

resulting in (15.15).

In gnomostereograms Problem 2 can be easily solved with the aid of the Wulff net: rotating the net about the centre of projection we find the arc of a great circle which can be drawn through two points corresponding to the projections of the specified faces.

Problem 3. **Let us find a face bounded by edges $[\boldsymbol{l}^1 \boldsymbol{l}^2 \boldsymbol{l}^3]$ and** $[\boldsymbol{k}^1 \boldsymbol{k}^2 \boldsymbol{k}^3]$. Reasoning as in Problem 2 we find that a normal to the sought for face $\boldsymbol{n}$ is perpendicular to both edges. We shall again determine its direction from the corresponding vector product, this time, however, not multiplied but divided by the unit cell volume:

$$\boldsymbol{n} = \frac{1}{v} \boldsymbol{l} \times \boldsymbol{k}. \tag{15.18}$$

Substitute the expanded expressions for vectors $\boldsymbol{l}$ and $\boldsymbol{k}$:

$$\begin{aligned} \boldsymbol{l} &= l^1 \boldsymbol{a}_1 + l^2 \boldsymbol{a}_2 + l^3 \boldsymbol{a}_3 = l^\alpha \boldsymbol{a}_\alpha, \\ \boldsymbol{k} &= k^1 \boldsymbol{a}_1 + k^2 \boldsymbol{a}_2 + k^3 \boldsymbol{a}_3 = k^\alpha \boldsymbol{a}_\alpha \end{aligned} \tag{15.19}$$

and, just as in the preceding problem, perform a term-by-term vector multiplication. Vector products of base vectors divided by the crystallographic cell volume are equal to corresponding base vectors of

a reciprocal lattice (see Sec. 11). Thus we obtain

$$\boldsymbol{n} = (l^2k^3 - l^3k^2)\,\boldsymbol{a}^1 + (l^3k^1 - l^1k^3)\,\boldsymbol{a}^2 + (l^1k^2 - l^2k^1)\,\boldsymbol{a}^3, \quad (15.20)$$

so that indices $(n_1n_2n_3)$ are determined by formulas similar to (15.15):

$$n_1 = l^2k^3 - l^3k^2, \quad n_2 = l^3k^1 - l^1k^3, \quad n_3 = l^1k^2 - l^2k^1, \quad (15.21)$$

which are very much like (15.15). Using the Levi-Civita symbol, we obtain similarly to (15.17)

$$n_\alpha = \delta_{\alpha\beta\gamma} l^\beta k^\gamma. \quad (15.22)$$

This problem can also be solved by cross-multiplication, as in Problem 2.

In gnomostereograms Problem 3 is also solved with the aid of the Wulff net: the intersection of two arcs of a great circle, which are the projections of edges, will give the point of the projection of the face bounded by the two edges.

In stereograms the last two problems are also solved with the aid of the Wulff net, with the only difference that the projections of planes will be arcs and those of directions, points (see Sec. 2).

The above methods of solution are applicable to the Miller indices. If the faces and edges are specified by the Bravais indices, it is necessary to change to the Miller indices by means of formulas given in the preceding Sections, and having obtained a solution to change back to the Bravais indices.

Problem 4. **Hexagonal crystals (calculations are done with Bravais indices).** If not the Miller indices, but the Bravais ones are given, one should, generally speaking, change from the latter to vector notation of crystallographic planes and directions (by methods explained in Sec. 12), then solve the required problem, and thereupon return to the Bravais indices. For the most frequently occurring problems it is not difficult, however, to derive calculation formulas directly in the Bravais indices. Let us derive three of such formulas.

The condition for the direction (edge) with the Bravais indices $[r^1r^2r^3r^4]$ to belong to the plane (face) with Bravais indices $(p^1p^2p^3p^4)$ is

$$r^1p_1 + r^2p_2 + r^3p_3 + r^4p_4 = 0. \quad (15.23)$$

If the Bravais indices of two crystal faces are $(p_1p_2p_3p_4)$ and $(q_1q_2q_3q_4)$, then Bravais indices of their intersection edge are specified by the relation

$$r^1 : r^2 : r^3 : r^4 =$$
$$[(p_2 - p_3)\,q_4 - (q_2 - q_3)\,p_4] : [(p_3 - p_1)\,q_4 - (q_3 - q_1)\,p_4] :$$
$$: [(p_1 - p_2)\,q_4 - (q_1 - q_2)\,p_4] : 3\,(p_1q_2 - p_2q_1). \quad (15.24)$$

If the Bravais indices of two edges (directions) of a crystal are $[r^1r^2r^3r^4]$ and $[s^1s^2s^3s^4]$, then the indices of the face (plane) defined

by these edges are

$$p_1 : p_2 : p_3 : p_4 = [(r^2-r^3)\,s^4-(s^2-s^3)\,r^4] : [(r^3-r^1)\,s^4-(s^3-s^1)\,r^4] : [(r^1-r^2)\,s^4-(s^1-s^2)\,r^4] : [(r^2-r^3)\,(s^3-s^1)-(s^2-s^3)\,(r^3-r^1)]. \tag{15.25}$$

Problem 5. **Calculation of the length of vectors of direct and reciprocal lattices.** Even more complicated problems of geometric crystallography, particularly, those connected with the calculation of scalar products, can be solved with the use of the metric tensor of a lattice.

The use a of metric tensor for these problems is based on the fact that if only the contravariant components of two vectors are known, it is not possible to calculate their scalar product: it is necessary to know the covariant components of the metric tensor too. Thus, the scalar product of two vectors, $\boldsymbol{k}^1 = k^\alpha \boldsymbol{a}_\alpha$ and $\boldsymbol{l} = l^\beta \boldsymbol{a}_\beta$ specified by their contravariant components k^α and l^β is $\boldsymbol{k}\cdot\boldsymbol{l} = k^\alpha l^\beta \boldsymbol{a}_\alpha \cdot \boldsymbol{a}_\beta$. But according to (11.11) $\boldsymbol{a}_\alpha \cdot \boldsymbol{a}_\beta = g_{\alpha\beta}$, therefore

$$\boldsymbol{k}\cdot\boldsymbol{l} = g_{\alpha\beta} k^\alpha l^\beta. \tag{15.26}$$

Hence follows the method of calculating the length of a vector specified by its contravariant components:

$$l = \sqrt{\boldsymbol{l}\cdot\boldsymbol{l}} = \sqrt{g_{\alpha\beta} l^\alpha l^\beta}. \tag{15.27}$$

If vectors are specified by covariant components, then in similar formulas not the covariant but the contravariant components of the metric tensor will appear: the scalar product of vectors $\boldsymbol{m} = m_\alpha \boldsymbol{a}^\alpha$ and $\boldsymbol{n} = n_\beta \boldsymbol{a}^\beta$ is equal to $\boldsymbol{m}\cdot\boldsymbol{n} = m_\alpha \cdot n_\beta \boldsymbol{a}^\alpha \cdot \boldsymbol{a}^\beta$ or

$$\boldsymbol{m}\cdot\boldsymbol{n} = g^{\alpha\beta} m_\alpha n_\beta, \tag{15.28}$$

and the length of vector $\boldsymbol{n}$ specified by its covariant components n_α, is

$$n = \sqrt{g^{\alpha\beta} n_\alpha n_\beta}. \tag{15.29}$$

If, however, both co- and contravariant components of vectors are known, the scalar products and lengths are calculated without the metric tensor. For instance, $\boldsymbol{l}\cdot\boldsymbol{n} = l^\alpha n_\alpha$.

Problem 6. **Interplanar distances.** The length n of the reciprocal lattice vector $\boldsymbol{n} = n_\alpha \boldsymbol{a}^\alpha$ is the inverse of the interplanar distance of a system of parallel planes $(n_1 n_2 n_3)$ interconnected by translation which is determined by the vector $\boldsymbol{n}$. Thus the interplanar distance $d\,(\boldsymbol{n})$ is defined as

$$d\,(\boldsymbol{n}) = (g^{\alpha\beta} n_\alpha n_\beta)^{-1/2} \tag{15.30}$$

which follows from (15.29). In the determination of interplanar distances in non-primitive (centred) lattices not only the metric tensor

of a centred lattice can be used, but also the metric tensor of a corresponding primitive lattice. In the latter case it should be borne in mind that planes passing through centering points are denoted by Miller indices permitting contraction. Thus, in a face-centred cubic lattice planes (200) and (220) pass through the centering points; the respective interplanar spacings $d_{(200)} = a/2$, $d_{(220)} = a\sqrt{2}/4$ are, as would be expected, twice smaller than the similar interplanar distances in a simple cubic lattice with the same parameter a, i.e.

$$d_{(100)} = a, \quad d_{(110)} = a\sqrt{2}/2.$$

Problem 7. **Calculation of angles between crystallographic directions and planes.** If the projections of these directions or planes are known, the problem is easily solved with the aid of the Wulff net. Angular distances between two points on a sphere are measured along the arcs of great circles. If both points (projections of directions in stereograms or planes in gnomostereograms) lie on the same hemisphere, then rotating the net (or the tracing paper on which the projection is drawn), we bring the two points to one meridian and measure the angle along it. If the points are in different hemispheres, we bring them to the meridians symmetric with respect to the centre of the net and measure the angle along one meridian from the point to the pole, and along the other from the pole to the point.

Let us solve this problem analytically. Crystallographic directions $[k^1k^2k^3]$ and $[l^1l^2l^3]$ correspond to vectors $\boldsymbol{k} = k^\alpha \boldsymbol{a}_\alpha$ and $\boldsymbol{l} = l^\beta \boldsymbol{a}_\beta$; the cosine of the angle between them $\cos\varphi = \boldsymbol{k}\cdot\boldsymbol{l}/(kl)$ is calculated as

$$\cos\varphi = \frac{g_{\alpha\beta}k^\alpha l^\beta}{\sqrt{(g_{\gamma\eta}k^\gamma k^\eta)(g_{\xi\zeta}l^\xi l^\zeta)}}. \tag{15.31}$$

Angle ψ between perpendiculars to crystallographic planes $(m_1m_2m_3)$ and $(n_1n_2n_3)$ is calculated by a similar formula

$$\cos\psi = \frac{g^{\alpha\beta}m_\alpha n_\beta}{\sqrt{(g^{\gamma\xi}m_\gamma m_\xi)(g^{\eta\zeta}n_\eta n_\zeta)}}. \tag{15.32}$$

For calculating the angle χ between the crystallographic direction $[l^1l^2l^3]$ and the perpendicular to crystallographic plane $(n_1n_2n_3)$ it is also necessary to know the components of the metric tensor:

$$\cos\chi = \frac{l^\alpha_{n\alpha}}{\sqrt{(g_{\beta\gamma}l^\beta l^\gamma)(g^{\xi\eta}n_\xi n_\eta)}}. \tag{15.33}$$

For calculating all these angles it is not at all necessary to know the dimensions of the cell, it will suffice to know its exact form. In other words, it is not necessary to know all the components of the metric tensor, it is sufficient to know their ratios. In particular, the forms of unit cells of the rhombohedral and hexagonal lattices

are determined by a single parameter. Let us discuss this question in more detail.

Problem 8. **Axial ratios.** The metric tensor of the rhombohedral system of coordinates $g_{\alpha\beta}$ with a generally accepted unit cell has a matrix

$$G = \begin{Vmatrix} b^2 & b^2\cos\alpha & b^2\cos\alpha \\ b^2\cos\alpha & b^2 & b^2\cos\alpha \\ b^2\cos\alpha & b^2\cos\alpha & b^2 \end{Vmatrix}, \tag{15.34}$$

where b is the length of the edge of a unit rhombohedron, α is the angle at the vertex of the rhombohedron between its adjacent edges (see Appendix B). Evidently, the form of the rhombohedron (as distinct from its size) is specified exactly by the angle α.

The metric tensor of the hexagonal system of coordinates, which we denote by $g_{\alpha'\beta'}$ has a matrix

$$G' = \begin{Vmatrix} a^2 & -a^2/2 & 0 \\ -a^2/2 & a^2 & 0 \\ 0 & 0 & c^2 \end{Vmatrix}, \tag{15.35}$$

where a is the length of the cell edges lying in the basal plane, c is the length of the edge parallel to the principal symmetry axis. The form of the cell is specified by the axial ratio c/a.

As was shown in Sec. 13, a crystal of the trigonal system can be described both in the hexagonal and in the rhombohedral system of coordinates. In the first case its lattice will be specified by the axial ratio c/a, in the second by the angle α at the vertex of the rhombohedron. Let us find the relation connecting the parameters c/a and α in the case when they specify one and the same crystal.

Metric tensors (15.34) and (15.35) are connected by relation (13.23) where $\| P^{\alpha}_{\gamma'} \|$ is the matrix of the change from the rhombohedral system of coordinates to the hexagonal one (13.29). Let us calculate $g_{1'1'} = a^2$ and $g_{3'3'} = c^2$. Let us write in detail the calculations for $g_{1'1'}$. According to (13.23), $g_{1'1'} = P^{\alpha}_{1'}P^{\beta}_{1'}g_{\alpha\beta}$, or written in full

$$g_{1'1'} = (P^1_{1'})^2 g_{11} + (P^2_{1'})^2 g_{22} + (P^3_{1'})^2 g_{33} + \\ + 2P^2_{1'}P^3_{1'}g_{23} + 2P^3_{1'}P^1_{1'}g_{31} + 2P^1_{1'}P^2_{1'}g_{12}$$

(the metric tensor symmetry has been used here). Noting that $P^1_{1'} = -P^2_{1'} = 1$ and $P^3_{1'} = 0$, we obtain

$$g_{1'1'} = g_{11} + g_{22} - 2g_{12},$$

and substituting the values of the metric tensor components from (15.34) and (15.35) we shall have

$$a^2 = 2b^2(1 - \cos\alpha).$$

Upon similar calculations from formula $g_{3'3'} = P^{\alpha}_{3'} P^{\beta}_{3'} g_{\alpha\beta}$ we obtain $c^2 = 3b^2 (1 + 2 \cos \alpha)$.

Thus, the relation sought for will appear:

$$\frac{c}{a} = \sqrt{\frac{3(1+2\cos\alpha)}{2(1-\cos\alpha)}}, \quad \cos\alpha = \frac{2(c/a)^2 - 3}{2(c/a)^2 + 6}. \qquad (15.36)$$

Rhombohedrons are naturally divided into extended (acute) ones with an acute angle at the vertex and oblate (obtuse) ones with an obtuse angle at the vertex; the rhombohedron intermediate between them with a right angle at the vertex is simply a cube. The angle $\alpha = 90°$ and the axial ratio $c/a = \sqrt{3/2} \approx 1.225$ correspond to it.

Besides a cube, there are two more rhombohedrons which can serve as primitive cells of the cubic crystal lattice: first, an extended rhombohedron with an angle at the vertex $\alpha = \arccos(1/2) = 60°$, to which corresponds the axial ratio $c/a = \sqrt{6} \approx 2.449$, a primitive cell of the face-centred cubic lattice, and second, an oblate rhombohedron with angle $\alpha = \arccos(-1/3) \approx 109°28'$ and axial ratio $c/a = \sqrt{3/8} \approx 0.6124$, a primitive cell of the body-centred cubic lattice. These results immediately follow from the corresponding metric tensors (see Appendix B).

Knowing what axial ratio should be ascribed to the body-centred cubic lattice considered in the hexagonal aspect, it will be easy to calculate the axial ratio for a lattice corresponding to a hexagonal close packing. Indeed, in both cases we have to deal with similar close-packed layers lying in the basal plane, but the period of identity in the direction perpendicular to the plane consists of three such layers in the face-centred cubic lattice, while in the hexagonal close packing there are only two layers. Hence it follows that the axial ratio of the hexagonal close packing is two-thirds of the axial ratio of the face-centred cubic lattice, i.e. $c/a = 2\sqrt{6}/3 \approx 1.633$.

Crystallography and different aspects of the study of crystal symmetry are described in greater detail in the following books:

Some more details on crystallography and various aspects of the science of the symmetry of crystals can be found in the following books: N. V. Belov (1947, 1951, 1976); Bokyi (1971); Boldyrev (1934); Varikash and Khachatryan (1969); Vasiliev (1972); Delone, Padurov, Alexandrov (1934); Zhdanov (1961); Zagalskaya and Litvinskaya (1973, 1976); Koptsik (1966); Kostov (1965); Popov and Shafranovsky (1972); E. S. Fedorov (1949); Flint (1956); Shaskolskaya (1957, 1976, 1978, 1978a); Shafranovsky (1968, 1968a); Shubnikov (1940, 1940a, 1951); Shubnikov, Flint and Bokyi (1940); Shubnikov and Koptsik (1972); Buerger (1942, 1965, 1970); Burkhardt (1947); International Tables (1965, 1972); Bhagavantam, Venkatarayudu (1959); Kleber (1977); Lipson, Cochran (1966); Lonsdale (1948); Phillips (1971); Weyl (1952).

Chapter II

COORDINATE SYSTEMS, VECTORS AND TENSORS

Sec. 16. Cartesian Coordinate Systems

Crystallographic coordinate systems have the remarkable property of specifying crystallographic planes and directions by means of vectors with integral components. However, in many branches of crystal physics this property is not essential, while the dependence of vector or tensor components, characterizing a physical field (electric, magnetic, or a field of a mechanical stress), not only on the field strength but also on the parameters of a crystal unit cell appears to be a grave disadvantage. Therefore preference is given in crystal physics to *Cartesian* systems of coordinates, all base vectors of which are of unit length and orthogonal in pairs. Such bases are called *orthonormalized.* We denote the base vectors by $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$ and call them unit vectors. If letter indices are necessary, we use not Greek but Latin letters: i, j, k, l, m, $n = 1, 2, 3$. The scalar product of any such base vector multiplied by itself is unity, and by any other base vector, it is zero, i.e.

$$\boldsymbol{e}_i \cdot \boldsymbol{e}_k = \delta_{ik}. \tag{16.1}$$

This means that for Cartesian coordinates not only the mixed but also the covariant components of a metric tensor are defined by Kronecker's symbol

$$g_{ik} = \delta_{ik} \tag{16.2}$$

Thus, in an orthonormalized basis matrix G (and its inverse matrix G^{-1}) consisting of covariant components g_{ik} (and contravariant ones g^{ik}) of a metric tensor coincides with a unit matrix. Hence another important characteristic property of an orthonormalized basis: its reciprocal basis coincides with it:

$$\boldsymbol{e}^1 = \boldsymbol{e}_1, \quad \boldsymbol{e}^2 = \boldsymbol{e}_2, \quad \boldsymbol{e}^3 = \boldsymbol{e}_3. \tag{16.3}$$

Since the contravariant base vectors do not differ from the covariant ones, the contravariant components of vectors obviously do not differ from the covariant ones. This being the case, all indices can be written on the same level (it is standard to write them as subscripts) and, accordingly, any indices twice repeated can be regarded as summation indices. Components l_i of any vector with respect to the crystal-physical system of coordinates, equal to the scalar products of

the vector by the corresponding unit vectors

$$l_i = \boldsymbol{l} \cdot \boldsymbol{e}_i, \tag{16.4}$$

no longer depend on the parameters of the crystal unit cell: since $\boldsymbol{e}_i$ is a unit vector, each component l_i is fully defined by the length l of vector $\boldsymbol{l}$ and the angle φ_i it makes up with the respective coordinate axis X_i:

$$l_i = l \cos \varphi_i. \tag{16.5}$$

The calculation of the scalar and vector products of vectors, and all the quantities connected with them, is greatly simplified in the Cartesian coordinates. Indeed, in terms of the components we have for the scalar product of vectors $\boldsymbol{p}$ and $\boldsymbol{q}$ in the Cartesian system

$$\boldsymbol{p} \cdot \boldsymbol{q} = p_i q_i; \tag{16.6}$$

for the length of vector $\boldsymbol{p}$

$$p = \sqrt{p_i p_i}; \tag{16.7}$$

for the angle φ between vectors $\boldsymbol{p}$ and $\boldsymbol{q}$:

$$\varphi = \arccos \frac{p_i q_i}{\sqrt{p_j p_j q_k q_k}}. \tag{16.8}$$

The components of the vector product $\boldsymbol{s} = \boldsymbol{p} \times \boldsymbol{q}$ are calculated according to expression

$$s_i = \delta_{ijk} p_j q_k \tag{16.9}$$

which can also be written as

$$\boldsymbol{s} = \delta_{ijk} p_j q_k \boldsymbol{e}_i. \tag{16.10}$$

Hence it can be easily deduced that the mixed product of three vectors is

$$\boldsymbol{r} (\boldsymbol{p} \times \boldsymbol{q}) = \delta_{ijk} r_i p_j q_k. \tag{16.11}$$

The Cartesian system of coordinates, conventionally oriented with respect to the crystallographic system, is called the *crystal-physical system of coordinates*; the orientation of axes in crystal-physical coordinates for all classes of crystal symmetry is given in Appendix A.

Let us assume that each of the coordinate systems we are concerned with is given by its basis: the crystallographic one by the base lattice vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, the crystal-physical one by mutually orthogonal unit vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$. The relation between crystal-physical and crystallographic systems of coordinates is well-defined by the coefficients in the expansion of the vectors of one basis into the vectors of another basis: for resolving the base lattice vectors into unit vectors of the crystal-physical system of coordinates

$$\boldsymbol{a}_\alpha = A_{\alpha i} \boldsymbol{e}_i \tag{16.12}$$

or, vice versa, for resolving these unit vectors into the base lattice vectors

$$e_i = E_i^\alpha a_\alpha. \tag{16.13}$$

Matrices $\| A_{\alpha i} \|$ and $\| E_i^\alpha \|$ composed of the expansion coefficients are mutually reciprocal:

$$A_{\alpha i} E_i^\beta = \delta_\alpha^\beta, \quad E_i^\alpha A_{\alpha j} = \delta_{ij}. \tag{16.14}$$

According to definition (see Sec. 11), the covariant components of a metric tensor are $g_{\alpha\beta} = a_\alpha \cdot a_\beta$. Substituting (16.12), we obtain

$$g_{\alpha\beta} = A_{\alpha i} A_{\beta i}. \tag{16.15}$$

Similarly, we find

$$g^{\alpha\beta} = E_i^\alpha E_i^\beta. \tag{16.16}$$

According to (13.14), the determinant of the transition matrix from one basis to another is equal to the ratio of the cell volumes constructed on base vectors. Therefore

$$\det \| A_{\alpha i} \| = v, \quad \det \| E_i^\alpha \| = 1/v \tag{16.17}$$

where v is the volume of a unit cell. Since according to (16.15), $\det G = (\det \| A_{\alpha i} \|)^2$, then

$$\det G = v^2. \tag{16.18}$$

Transition from the crystallographic coordinates to the crystal-physical ones, as well as a reverse transition, is a special case of transition from one vector basis to another, discussed in detail in Sec. 13. It should only be noted that in the crystallographic system of coordinates the directions and planes are given by vectors $l = l^\alpha a_\alpha$ and $n = n_\alpha a^\alpha$ whose lengths are defined by the demand that the components l^α and n_α be integers and have no common factors. Conversely, in the crystal-physical coordinate systems all directions are conventionally given by unit vectors, so that l_i and n_i are the components of unit vectors characteristic of the corresponding directions. Tabulated, the above appears as follows:

Quantities compared	Transition from the crystallographic to the crystal-physical system	Transition from the crystal-physical to the crystallographic system
Base lattice vectors a_α and mutually orthogonal unit vectors e_i	$e_i = E_i^\alpha a_\alpha$	$a_\alpha = A_{\alpha i} e_i$
Base reciprocal lattice vectors a^α and mutually orthogonal unit vectors e_i	$e_i = A_{\alpha i} a^\alpha$	$a^\alpha = E_i^\alpha e_i$

Quantities compared	Transition from the crystallographic to the crystal-physical system	Transition from the crystal-physical to the crystallographic system
Indices of planes (faces) n_α and components of a unit vector n_i	$n_i = \dfrac{E_i^\alpha n_\alpha}{\sqrt{g^{\beta\gamma} n_\beta n_\gamma}}$	$n_\alpha = \lambda A_{\alpha i} n_i$
Indices of directions (edges) l^α and components of a unit vector l_i	$l_i = \dfrac{A_{\alpha i} l^\alpha}{\sqrt{g_{\beta\gamma} l^\beta l^\gamma}}$	$l^\alpha = \lambda E_i^\alpha l_i$

Coefficient λ should be selected so that indices are integers and have no common factors.

Matrices $\| A_{\alpha i} \|$ and $\| E_i^\alpha \|$ for all the crystallographic systems are given in Appendix B.

Sec. 17. Orthogonal Transformations

To solve crystal-physical problems it is sometimes convenient to use not the crystal-physical but some other system of Cartesian coordinates, the directions of whose axes are specified by the geometry of the problem. The system of Cartesian coordinates being fully specified by its orthonormalized basis, the transformation of the Cartesian coordinates means a transition from one orthonormalized basis to another.

The transformation in which one orthonormalized basis changes into another, also orthonormalized, is called an *orthogonal transformation*. A set of all such transformations forms an orthogonal group $\infty\infty m$. Transformations included in the orthogonal group—orthogonal transformations—do not change either the length of the vectors, or the angles between them, which allows an orthonormalized basis to remain orthonormalized under transformation.

Let us note for comparison that, performing the transformation of crystal lattice bases, we did not require their being orthogonal, e.g. in the transformation from a rhombohedral basis to the hexagonal one, both the lengths of base vectors and the angles between them were changed.

Let the "old" system of coordinates, X_1, X_2, X_3 be constructed on the basis $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$, while the "new" one $X_{1'}$, $X_{2'}$, $X_{3'}$, on the basis $\boldsymbol{e}_{1'}$, $\boldsymbol{e}_{2'}$, $\boldsymbol{e}_{3'}$. The expansion of the new basis into vectors of the old one

$$\boldsymbol{e}_{i'} = c_{i'k} \boldsymbol{e}_k \tag{17.1}$$

is defined by coefficients $c_{i'k}$ which form the *matrix of the orthogonal transformation*

$$\| c_{i'k} \| = \begin{Vmatrix} c_{1'1} & c_{1'2} & c_{1'3} \\ c_{2'1} & c_{2'2} & c_{2'3} \\ c_{3'1} & c_{3'2} & c_{3'3} \end{Vmatrix}.$$

It is also called a *cosine matrix*, since each element $c_{i'k}$ is the cosine of the angle between two corresponding coordinate axes (Fig. 17.1):

$$c_{i'k} = \boldsymbol{e}_{i'} \cdot \boldsymbol{e}_k = \cos(X_{i'}, X_k) = \cos \alpha_{i'k}. \tag{17.2}$$

An inverse transformation

$$\boldsymbol{e}_k = c_{ki'} \boldsymbol{e}_{i'}, \tag{17.3}$$

is apparently characterized by matrix $\| c_{ki'} \|$ which is simultaneously both the inverse of the initial marxix $\| c_{i'k} \|$ and its *transpose*. Such matrices satisfy the relations

$$c_{i'k} c_{j'k} = \delta_{i'j'}, \quad c_{i'k} c_{i'l} = \delta_{kl} \tag{17.4}$$

and are called *orthogonal*. The square of the determinant of such a matrix is unity, or

$$\Delta = \det \| c_{i'k} \| = \pm 1. \tag{17.5}$$

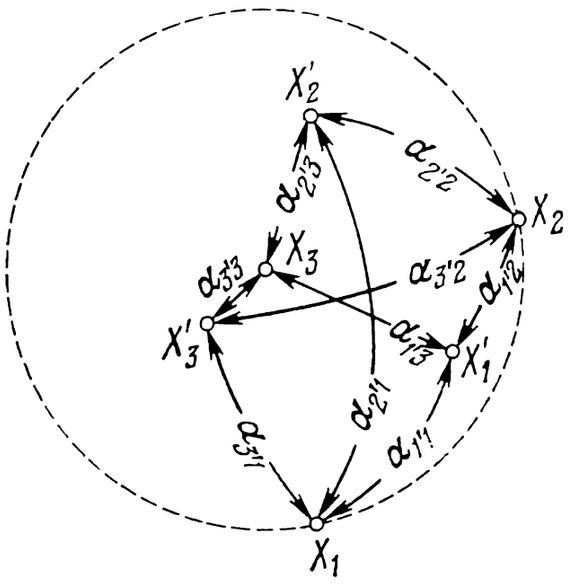


Fig. 17.1. Angles α_{ik} between "old" and "new" coordinate axes, a stereogram

The orthogonal transformation can be divided into *proper* rotation and *improper* rotation, or rotation with reflexion. To the former there correspond matrices with a determinant $+1$, and to the latter those with a determinant -1.

Any rotation R can be specified by a rotation axis and the angle of rotation about it. Therefore, to specify any rotation, it will suffice to have one vector $\boldsymbol{\varphi}$ whose direction coincides with the axis of rotation, and length φ is equal to the angle of rotation. Let us agree that rotation $R(\boldsymbol{\varphi})$ about vector $\boldsymbol{\varphi}$ will be right-handed. All the imaginable rotations will be taken account of, if all possible vectors $\boldsymbol{\varphi}$ whose lengths satisfy inequalities $0 \leqslant \varphi \leqslant \pi$ are considered. To every rotation by an angle less than π there will be a unique corresponding vector, while to rotation by angle π there will be two corresponding vectors of equal length but of opposite directions. Rotation $R(\boldsymbol{\varphi})$ is more often denoted by $R(\boldsymbol{k}, \varphi)$, where $\boldsymbol{k} = \boldsymbol{\varphi}/\varphi$ is the unit vector directed along vector $\boldsymbol{\varphi}$.

If a new Cartesian system of coordinates constructed on the orthonormalized basis $\boldsymbol{e}_{1'}$, $\boldsymbol{e}_{2'}$, $\boldsymbol{e}_{3'}$, has been obtained from an old system constructed on the basis $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$ by means of rotation $R(\boldsymbol{k}, \varphi)$, then matrix $\| r_{i'j}(\boldsymbol{k}, \varphi) \|$, corresponding to this rotation, i.e. specifying the expansion $\boldsymbol{e}_{i'} = r_{i'j}\boldsymbol{e}_j$, appears as follows*

$$\| r_{i'j}(k, \varphi) \| =$$

$$= \begin{Vmatrix} \cos\varphi + k_1^2(1-\cos\varphi) & k_3\sin\varphi + k_1k_2(1-\cos\varphi) & -k_2\sin\varphi + k_1k_3(1-\cos\varphi) \\ -k_3\sin\varphi + k_2k_1(1-\cos\varphi) & \cos\varphi + k_2^2(1-\cos\varphi) & k_1\sin\varphi + k_2k_3(1-\cos\varphi) \\ k_2\sin\varphi + k_3k_1(1-\cos\varphi) & -k_1\sin\varphi + k_3k_2(1-\cos\varphi) & \cos\varphi + k_3^2(1-\cos\varphi) \end{Vmatrix}.$$

With the aid of the Kronecker and Levi-Civita symbols its elements are written thus:

$$r_{i'j}(\boldsymbol{k}, \varphi) = \delta_{i'j}\cos\varphi + \delta_{i'jl}k_l\sin\varphi + k_{i'}k_j(1-\cos\varphi). \qquad (17.6)$$

In (17.6) $k_{i'}$ and k_j are the components of vector $\boldsymbol{k}$ in the new and old systems respectively, but since one system is obtained from the other by rotation about this particular vector, the components simply coincide: $k_{1'} = k_1$, $k_{2'} = k_2$, $k_{3'} = k_3$. For small ($\varphi \ll 1$) angles of rotation

$$r_{i'j}(\varphi) \approx \delta_{i'j} + \delta_{i'jk}\varphi_k. \qquad (17.7)$$

Inverse rotation through angle φ about the unit vector $\boldsymbol{k}$ is the product of a corresponding rotation by inversion: $Q(\boldsymbol{k}, \varphi) = \bar{I}\cdot R(\boldsymbol{k}, \varphi)$. Consequently, its matrix $\| q_{i'j}(\boldsymbol{k}, \varphi) \|$ is the product of matrix $\| r_{i'j}(\boldsymbol{k}, \varphi) \|$ by the inversion matrix $\| -\delta_{i'j} \|$, i.e. $\| q_{i'j}(\boldsymbol{k}, \varphi) \| = \| -r_{i'j}(\boldsymbol{k}\varphi) \|$. Thus, the matrix of the orthogonal transformation generally appears as

$$c_{i'j}(\boldsymbol{k}, \varphi) = \Delta\,[\delta_{i'j}\cos\varphi + \delta_{i'jl}k_l\sin\varphi + k_{i'}k_j(1-\cos\varphi)] \qquad (17.8)$$

where $\Delta = \pm 1$; $\Delta = +1$ corresponds to proper rotation and $\Delta = -1$ to the inverse one.

Table 17.1 shows the matrices of crystallographic transformations of symmetry, both for general and for a particular selection of rotation axes, most frequently used in crystallography and crystal physics.

The *trace*, i.e. the sum of the diagonal elements of matrix $\| c_{i'j}(k, \varphi) \|$, is denoted** Tr $\| c_{i'j} \|$ and is equal to $c_{jj} = \Delta(1 + 2\cos\varphi)$. Hence

$$\cos\varphi = \frac{1}{2}(\Delta c_{jj} - 1). \qquad (17.9)$$

---

* To derive the first row of this matrix it will suffice to find vector $\boldsymbol{e}_{1'}$, which results from the rotation of vector $\boldsymbol{e}_1$ about $\boldsymbol{k}$ through angle φ, and to calculate the scalar products $\boldsymbol{e}_{1'}\cdot\boldsymbol{e}_j$. The second and the third rows are easily obtained from the first one by cyclic substitution.

** Or Sp, from the German word "Spur" which also means "trace".

Table 17.1

Matrices of Crystallographic and Limit Symmetry Transformations in Cases of Arbitrary and Specific Selection of the Unit Vector k of the Rotation Axis

	1	$\bar{1}$
	$\begin{Vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{Vmatrix}$	$\begin{Vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{Vmatrix}$
	2	m
	$\begin{Vmatrix} 2k_1^2-1 & 2k_1k_2 & 2k_3k_1 \\ 2k_1k_2 & 2k_2^2-1 & 2k_2k_3 \\ 2k_3k_1 & 2k_2k_3 & 2k_3^2-1 \end{Vmatrix}$	$\begin{Vmatrix} 1-2k_1^2 & -2k_1k_2 & -2k_3k_1 \\ -2k_1k_2 & 1-2k_2^2 & -2k_2k_3 \\ -2k_3k_1 & -2k_2k_3 & 1-2k_3^2 \end{Vmatrix}$
$k=e_3$	$\begin{Vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{Vmatrix}$	$\begin{Vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{Vmatrix}$
$k=e_1$	$\begin{Vmatrix} 1 & 0 & 1 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{Vmatrix}$	$\begin{Vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{Vmatrix}$
$k=e_2$	$\begin{Vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{Vmatrix}$	$\begin{Vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{Vmatrix}$
$k=\dfrac{e_1+e_2}{\sqrt{2}}$	$\begin{Vmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{Vmatrix}$	$\begin{Vmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{Vmatrix}$
$k=\dfrac{e_1-e_2}{\sqrt{2}}$	$\begin{Vmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{Vmatrix}$	$\begin{Vmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{Vmatrix}$
$k=e_1\cos\psi+e_2\sin\psi$	$\begin{Vmatrix} \cos 2\psi & \sin 2\psi & 0 \\ \sin 2\psi & -\cos 2\psi & 0 \\ 0 & 0 & -1 \end{Vmatrix}$	$\begin{Vmatrix} -\cos 2\psi & -\sin 2\psi & 0 \\ -\sin 2\psi & \cos 2\psi & 0 \\ 0 & 0 & 1 \end{Vmatrix}$
	4	$\bar{4}$
	$\begin{Vmatrix} k_1^2 & k_1k_2+k_3 & k_3k_1-k_2 \\ k_1k_2-k_3 & k_2^2 & k_2k_3+k_1 \\ k_3k_1+k_2 & k_2k_3-k_1 & k_3^2 \end{Vmatrix}$	$\begin{Vmatrix} -k_1^2 & -k_3-k_1k_2 & k_2-k_3k_1 \\ k_3-k_1k_2 & -k_2^2 & -k_1-k_2k_3 \\ -k_2-k_3k_1 & k_1-k_2k_3 & -k_3^2 \end{Vmatrix}$
$k=e_3$	$\begin{Vmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{Vmatrix}$	$\begin{Vmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{Vmatrix}$

$$3 \qquad \begin{Vmatrix} \frac{3k_1^2-1}{2} & \frac{3k_1k_2+k_3\sqrt{3}}{2} & \frac{3k_3k_1-k_2\sqrt{3}}{2} \\ \frac{3k_1k_2-k_3\sqrt{3}}{2} & \frac{3k_2^2-1}{2} & \frac{3k_2k_3+k_1\sqrt{3}}{2} \\ \frac{3k_3k_1+k_2\sqrt{3}}{2} & \frac{3k_2k_3-k_1\sqrt{3}}{2} & \frac{3k_3^2-1}{2} \end{Vmatrix} \qquad \bar{3} \qquad \begin{Vmatrix} \frac{1-3k_1^2}{2} & \frac{-k_3\sqrt{3}-3k_1k_2}{2} & \frac{k_2\sqrt{3}-3k_3k_1}{2} \\ \frac{k_3\sqrt{3}-3k_1k_2}{2} & \frac{1-3k_2^2}{2} & \frac{-k_1\sqrt{3}-3k_2k_3}{2} \\ \frac{-k_2\sqrt{3}-3k_3k_1}{2} & \frac{k_1\sqrt{3}-3k_2k_3}{2} & \frac{1-3k_3^2}{2} \end{Vmatrix}$$

$$\boldsymbol{k}=\boldsymbol{e}_3 \qquad \begin{Vmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{Vmatrix} \qquad \begin{Vmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{Vmatrix}$$

$$\boldsymbol{k}=\frac{\boldsymbol{e}_1+\boldsymbol{e}_2+\boldsymbol{e}_3}{\sqrt{3}} \qquad \begin{Vmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{Vmatrix} \qquad \begin{Vmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{Vmatrix}$$

$$\boldsymbol{k}=\frac{-\boldsymbol{e}_1+\boldsymbol{e}_2+\boldsymbol{e}_3}{\sqrt{3}} \qquad \begin{Vmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{Vmatrix} \qquad \begin{Vmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{Vmatrix}$$

$$6 \qquad \begin{Vmatrix} \frac{1+k_1^2}{2} & \frac{k_1k_2+k_3\sqrt{3}}{2} & \frac{k_3k_1-k_2\sqrt{3}}{2} \\ \frac{k_1k_2-k_3\sqrt{3}}{2} & \frac{1+k_2^2}{2} & \frac{k_2k_3+k_1\sqrt{3}}{2} \\ \frac{k_3k_1+k_2\sqrt{3}}{2} & \frac{k_2k_3-k_1\sqrt{3}}{2} & \frac{1+k_3^2}{2} \end{Vmatrix} \qquad \bar{6} \qquad \begin{Vmatrix} \frac{-1-k_1^2}{2} & \frac{-k_3\sqrt{3}-k_1k_2}{2} & \frac{k_2\sqrt{3}-k_3k_1}{2} \\ \frac{k_3\sqrt{3}-k_1k_2}{2} & \frac{-1-k_2^2}{2} & \frac{-k_1\sqrt{3}-k_2k_3}{2} \\ \frac{-k_2\sqrt{3}-k_3k_1}{2} & \frac{k_1\sqrt{3}-k_2k_3}{2} & \frac{-1-k_3^2}{2} \end{Vmatrix}$$

$$\boldsymbol{k}=\boldsymbol{e}_3 \qquad \begin{Vmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{Vmatrix} \qquad \begin{Vmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{Vmatrix}$$

$$R(\boldsymbol{e}_3, \varphi) \qquad \begin{Vmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{Vmatrix} \qquad \bar{1}\,R(\boldsymbol{e}_3, \varphi) \qquad \begin{Vmatrix} -\cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & -\cos\varphi & 0 \\ 0 & 0 & -1 \end{Vmatrix}$$

Since angle φ is within the limits $(0, \pi)$, formula (17.9) allows to determine it uniquely. Now it is simple enough to find the unit vector $\boldsymbol{k}$ of the rotation axis:

$$k_l = \frac{\Delta}{2 \sin \varphi} \delta_{li'j} c_{i'j}. \tag{17.10}$$

This expression can be used only when $\varphi \neq \pi$. If $\varphi = \pi$, it follows from Table 17.1 that the components k_l can be determined as

$$k_1 = \pm \sqrt{\frac{\Delta c_{1'1} + 1}{2}}, \quad k_2 = \pm \sqrt{\frac{\Delta c_{2'2} + 1}{2}}, \quad k_3 = \pm \sqrt{\frac{\Delta c_{3'3} + 1}{2}} \tag{17.11}$$

and the signs have to be chosen so that

$$k_{i'} k_j = \frac{1}{2} \Delta c_{i'j}. \tag{17.12}$$

Thus, knowing the axis and the magnitude of rotation, all elements of matrix $\| c_{i'j} \|$ can be calculated, and vice versa, knowing the elements of this matrix, the axis and the angle of rotation can be determined from (17.9)-(17.12).

The result of two consecutive orthogonal transformations—the transition from the old basis, $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$, to the new one $\boldsymbol{e}_{1'}$, $\boldsymbol{e}_{2'}$, $\boldsymbol{e}_{3'}$, and then from the new one to the "newest", $\boldsymbol{e}_{1''}$, $\boldsymbol{e}_{2''}$, $\boldsymbol{e}_{3''}$, can be written as $\boldsymbol{e}_{i''} = c_{i''k} \boldsymbol{e}_k$, matrix $C = \| c_{i''k} \|$ performing the direct transition from the old to the newest basis, being expressed by matrices of individual transitions $C^{(1)} = \| c_{j'k} \|$ and $C^{(2)} = \| c_{i''j'} \|$:

$$c_{i''k} = c_{i''j'} c_{j'k}. \tag{17.13}$$

This formula can be represented as a matrix equality $C = C^{(2)} C^{(1)}$, it being necessary to observe the sequence of the factors: the matrix corresponding to the transformation which is done first should be written further to the right.

The non-commutativeness of matrix multiplication reflects the non-commutativeness of orthogonal transformations: having done two orthogonal transformations first in one and then in another sequence, it is possible to obtain different results (if only the rotation axes do not coincide).

Successive transformations are effected, for instance, when specifying transitions from one coordinate system to another by means of Eulerian angles. Rotation changing the system $OX_1X_2X_3$ to system $OX'_1X'_2X'_3$ can be performed in the following sequence.

1. Let us draw an auxiliary axis Y_1 along the line of intersection of planes OX_1X_2 and $OX'_1X'_2$. Choose the positive direction on the Y_1 axis so that angle $\varphi = \angle X_1OY_1$ taken from X_1 to X_2 satisfies condition $0 \leqslant \varphi < \pi$. Rotation of the coordinate system $OX_1X_2X_3$ about

axis X_3 through angle φ will transform it into system $OY_1Y_2Y_3$. The matrix of this rotation is

$$R^{(\varphi)} = \begin{Vmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{Vmatrix}.$$

2. Rotation about axis Y_1 through angle $\vartheta = \angle X_3OX_3'$ (read off from X_3 to Y_2) transforms system $OY_1Y_2X_3$ into the system $OY_1'Y_2'Y_3'$. The matrix of this rotation is

$$R^{\vartheta} = \begin{Vmatrix} 1 & 0 & 0 \\ 0 & \cos\vartheta & -\sin\vartheta \\ 0 & \sin\vartheta & \cos\vartheta \end{Vmatrix}.$$

3. Finally, rotation about axis X_3' through angle ψ read off from Y_1 to Y_2' will transform the system $OY_1Y_2'X_3'$ into system, $OX_1'X_2'X_3'$. Its matrix is

$$R^{(\psi)} = \begin{Vmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{Vmatrix}.$$

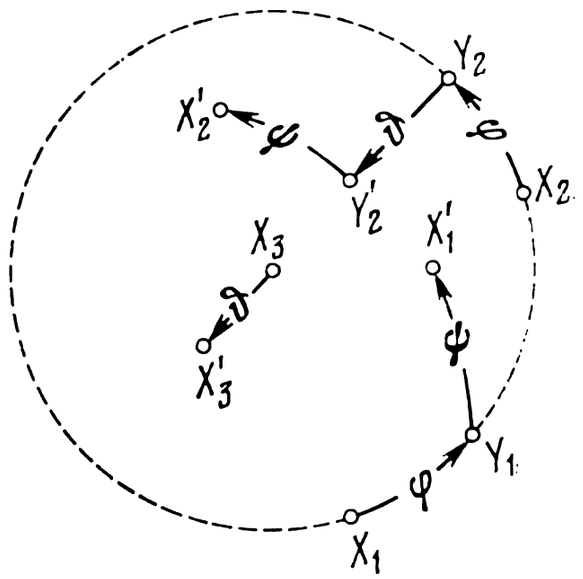


Fig. 17.2. Eulerian angles, a stereogram: $\varphi = 30°$, $\vartheta = 40°$, $\psi = 50°$

Obviously these three rotations can be replaced by one (Fig. 17.2) transforming system $OX_1X_2X_3$ into the $OX_1'X_2'X_3'$ one. The matrix of this rotation is $R = R^{(\psi)}R^{(\vartheta)}R^{(\varphi)}$. Having multiplied the matrices in the given sequence, we obtain

$$R = \begin{Vmatrix} \cos\varphi\cos\psi - & \sin\varphi\cos\psi + & -\sin\vartheta\sin\psi \\ -\sin\varphi\cos\vartheta\sin\psi & +\cos\varphi\cos\vartheta\sin\psi & \\ -\cos\varphi\sin\psi - & -\sin\varphi\sin\psi + & -\sin\vartheta\cos\psi \\ -\sin\varphi\cos\vartheta\cos\psi & +\cos\varphi\cos\vartheta\cos\psi & \\ -\sin\varphi\sin\vartheta & \cos\varphi\sin\vartheta & \cos\vartheta \end{Vmatrix}. \quad (17.14)$$

The three most frequently used methods of matrix calculation for the orthogonal transformations of coordinates were discussed above. If the angles between the new and old axes are known, formula (17.2) is used; if the transformation of the old system to the new one is known, formula (17.8) is used; and if the Eulerian angles are known, formula (17.14) is used.

Sec. 18. Second-Rank Tensors

It is known that under transition from one orthonormalized basis e_k to basis $e_{i'} = c_{i'k}e_k$ components v_k of vector v are transformed according to relations

$$v_{i'} = c_{i'k}v_k, \quad v_k = c_{i'k}v_{i'}. \tag{18.1}$$

Nine values T_{kl} transforming as the products of the components of two vectors, i.e. according to the relation

$$T_{i'j'} = c_{i'k}c_{j'l}T_{kl}, \quad T_{kl} = c_{i'k}c_{j'l}T_{i'j'}, \tag{18.2}$$

are called the *components of a second-rank tensor* **T**. Similarly, $3^3 = 27$ values of Q_{lmn} transforming as the products of the components of three vectors, i.e. according to expressions

$$Q_{i'j'k'} = c_{i'l}c_{j'm}c_{k'n}Q_{lmn}, \quad Q_{lmn} = c_{i'l}c_{j'm}c_{k'n}Q_{i'j'k'} \tag{18.3}$$

are called the *components of a third-rank tensor* **Q**, and so on.

Just as vector v is written in the form $v = v_i \cdot e_i$, its components being $v_i = v \cdot e_i$, so tensor **T** can be represented as*

$$\mathbf{T} = e_k T_{kl} e_l \tag{18.4}$$

(or $\mathbf{T}_{kl}e_k e_l$). Its components, T_{kl}, are calculated with respect to the basis e_k according to the formula:

$$T_{kl} = e_k \cdot \mathbf{T} \cdot e_l. \tag{18.5}$$

The components $T_{i'j'}$ of the same tensor, with respect to basis $e_{i'} = c_{i'k}e_k$ are $T_{i'j'} = e_{i'} \cdot \mathbf{T} \cdot e_{j'}$. If we substitute here (18.4) and note that $e_{i'} \cdot e_k = c_{i'k}$, we shall arrive at formula (18.2). This shows that the law of transformation (18.2) of the tensor components T_{kl} has been formulated so that the tensor $e_k T_{kl} e_l$ defined by these components is, like a vector, a geometric object, i.e. is independent of the coordinate system specifying it.

Second-rank tensors play different roles in crystal physics. The one is that of a linear operator mapping one set **u** onto another set $v = v(u)$ so that

$$v(\lambda u^{(1)} + \mu u^{(2)}) = \lambda v(u^{(1)} + \mu v(u^{(2)}), \tag{18.6}$$

where $u^{(1)}$ and $u^{(2)}$ are any vectors of the u set, while λ and μ are arbitrary real numbers. It follows from (18.6) that in any orthonormalized basis e_k the components v_k of vectors v are linear functions of the components u_l of the corresponding vectors u:

$$v_k = T_{kl}u_l. \tag{18.7}$$

In the basis $e_{i'} = c_{i'k}e_k$ this relation appears as $v_{i'} = \mathbf{T}_{i'j}u_{j'}$, and it follows, since vector components u_l and v_k transform according to

* Tensor of type $e_k e_l$ (in a general case ab) is called a *dyad*. Thus, in (18.4) tensor **T** is represented as a sum of nine dyads.

relations (18.1), that coefficients T_{kl} transform according to (18.2), i.e. that they are actually the components of the second-rank tensor **T**. Therefore relation (18.7) can be written in a non-coordinate form

$$\boldsymbol{v} = \mathbf{T}\cdot\boldsymbol{u}. \tag{18.8}$$

Let us discuss some special cases of linear transformations of vector sets. If vectors $\boldsymbol{v}$ are simply equal to vectors $\boldsymbol{u}$, the corresponding tensor is called a *unit tensor* and is denoted by **I**. Its components in any coordinate system are $I_{kl} = \sigma_{kl}$.

If vectors $\boldsymbol{v}$ are collinear with vectors $\boldsymbol{u}$ and are λ times longer, the linear dependence between $\boldsymbol{v}$ and $\boldsymbol{u}$ is shown by tensor $\lambda\mathbf{I}$ (such tensors are called *spherical* ones). A simpler expression $\boldsymbol{v} = \lambda\boldsymbol{u}$ is equivalent to $\boldsymbol{v} = \lambda\mathbf{I}\cdot\boldsymbol{u}$.

A component of any vector $\boldsymbol{u}$ parallel to some given unit vector $\boldsymbol{k}$ can be written as $\boldsymbol{kk}\cdot\boldsymbol{u}$. Thus tensor $\boldsymbol{kk}$ projects vectors on a line parallel to unit vector $\boldsymbol{k}$. Similarly, the projection of vectors on a plane perpendicular to unit vector $\boldsymbol{k}$ is performed by tensor $\mathbf{I} - \boldsymbol{kk}$.

The rotation of vectors through angle φ about axis $\boldsymbol{k}$ is done by tensor

$$\begin{gathered}\mathbf{R}(\boldsymbol{k}, \varphi) = \mathbf{I}\cos\varphi - \mathbf{I}\times\boldsymbol{k}\sin\varphi + \boldsymbol{kk}(1-\cos\varphi),\\ R_{ij} = \delta_{ij}\cos\varphi + \delta_{ijl}k_l\sin\varphi + k_ik_j(1-\cos\varphi).\end{gathered} \tag{18.9}$$

This follows from (17.6)*.

If the determinant of tensor **T** differs from zero, the linear dependence $\boldsymbol{v} = \mathbf{T}\cdot\boldsymbol{u}$ can be reversed to

$$\boldsymbol{u} = \mathbf{P}\cdot\boldsymbol{v}, \quad u_j = P_{jk}v_k.$$

The tensor **P** with the components

$$P_{jk} = \frac{\tau_{kj}}{\det\mathbf{T}}, \tag{18.10}$$

where τ_{kj} is the signed minor of element T_{kj} in the determinant $\det\|T_{il}\|$, is called the *inverse* of tensor **T**; this is denoted as $\mathbf{P} = \mathbf{T}^{-1}$. *Mutually reciprocal* tensors satisfy the following identities:

$$T_{ij}P_{jk} = \delta_{ik}, \quad P_{jk}T_{kl} = \delta_{jl}. \tag{18.11}$$

Tensors that project vectors onto a straight line and into a plane have no inverse tensors, while tensor $\mathbf{R}(\boldsymbol{k}, \varphi)$ that rotates vectors has its inverse tensor.

Second-rank tensors can be transposed like a matrix. If a tensor is not changed under transposition ($\mathbf{T}^* = \mathbf{T}$), it is called a *symmetric* one, if it changes its sign ($\mathbf{T}^* = -\mathbf{T}$), it is *antisymmetric*. Any tensor **T** can be resolved into a *symmetric part* $\mathbf{S} = 1/2\,(\mathbf{T} + \mathbf{T}^*)$ and

* Vector multiplication of tensor **T** by vector $\boldsymbol{v}$ is defined similarly to the scalar one: if $\mathbf{T} = \boldsymbol{e}_kT_{kl}\boldsymbol{e}_l$ then $\mathbf{T}\times\boldsymbol{v} = \boldsymbol{e}_kT_{kl}(\boldsymbol{e}_l\times\boldsymbol{v})$.

an *antisymmetric part* $\mathbf{A} = 1/2\ (\mathbf{T} - \mathbf{T}^*)$; their sum being equal to the initial tensor **T**.

A symmetric tensor S_{ij}, in its turn, can be resolved into a *spherical* part $1/3S_{kk}\delta_{ij}$ and a *deviator* $D_{ij} = S_{ij} - 1/3S_{kk}\delta_{ij}$. The trace of the spherical part is equal to the trace of the tensor, while the trace of the deviator is zero; in general, any symmetric second-rank tensor having a zero trace is called a *deviator*.

Second-rank tensors can be regarded not only as linear operators, but also as the result of differentiating a vector with respect to a vector or of a double differentiation of a scalar function with respect to a vector. Let us first discuss the simpler operation—the differentiation of a scalar function with respect to a vector. If f is a scalar function of components of vector $\boldsymbol{u}$ (and perhaps of other parameters), the quantities

$$v_k = \frac{\partial f}{\partial u_k} \tag{18.12}$$

are transformed as vector components. This permits rewriting (18.12) as

$$\boldsymbol{v} = \frac{\partial f}{\partial \boldsymbol{u}},$$

which emphasizes the independence of this operation from the choice of coordinates.

If, for instance, radius-vector $\boldsymbol{r}$ acts as a vector argument, $\boldsymbol{u}$, the derivative is called the gradient of function f and has a special notation $\boldsymbol{v} = \operatorname{grad} f$.

The derivative of a vector with respect to a vector is defined similarly. If the components of vector $\boldsymbol{v}$ are functions of the components of vector $\boldsymbol{u}$, the nine quantities

$$T_{kl} = \frac{\partial v_k}{\partial u_l} \tag{18.13}$$

are transformed as the components of a second-rank tensor. Therefore (18.13) can be written as

$$\mathbf{T} = \frac{\partial \boldsymbol{v}}{\partial \boldsymbol{u}}.$$

If radius-vector $\boldsymbol{r}$ serves as an argument, then

$$T = \frac{\partial \boldsymbol{v}}{\partial \boldsymbol{r}}, \quad T_{kl} = \left(\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{r}}\right)_{kl} = \frac{\partial v_k}{\partial x_l}.$$

However, not $\partial \mathbf{v}/\partial \mathbf{r}$ but the transpose of tensor

$$\operatorname{Grad} \boldsymbol{v} = \left(\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{r}}\right)^*, \qquad (\operatorname{Grad} \boldsymbol{v})_{kl} = \frac{\partial v_l}{\partial x_k},$$

is conventionally called the gradient of vector $\boldsymbol{v}$. The sum of the diagonal elements of these tensors is the divergence of vector $\boldsymbol{v}$:

$$\mathrm{Tr}\,\mathrm{Grad}\,\boldsymbol{v} = \mathrm{Tr}\left(\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{r}}\right) = \frac{\partial v_i}{\partial x_i} = \mathrm{div}\,\boldsymbol{v}.$$

The second derivative of a scalar function f with respect to its vector arguments $\boldsymbol{u}$ and $\boldsymbol{v}$ is also a second-rank tensor:

$$\mathbf{T} = \frac{\partial^2 f}{\partial \boldsymbol{u}\,\partial \boldsymbol{v}}, \quad T_{kl} = \frac{\partial^2 f}{\partial u_k \partial v_l}.$$

If it is a second derivative with respect to the same argument, i.e. $\mathbf{T} = \partial^2 f/\partial \boldsymbol{u}\,\partial \boldsymbol{u}$, then tensor $\mathbf{T}$ is symmetric.

Sec. 19. Eigenvectors and Eigenvalues of a Symmetric Second-Rank Tensor

A second-rank tensor $\mathbf{S}$ upon being scalarly multiplied by vector $\boldsymbol{u}$ transforms the latter into vector $\boldsymbol{v} = \mathbf{S}\cdot\boldsymbol{u}$. Vectors that do not change their direction under this operation, but merely become longer or shorter, are called *eigenvectors* of tensor $\mathbf{S}$ (Fig. 19.1). Hence they satisfy the equation

$$\boldsymbol{S}\cdot\boldsymbol{u} = S\boldsymbol{u}, \quad S_{ik}u_k = Su_i \tag{19.1}$$

where S is a number showing by how many times the length of vector $\mathbf{u}$ has been increased or decreased by the action of tensor $\mathbf{S}$ and is called the *eigenvalue* of tensor $\mathbf{S}$ corresponding to the given eigenvector.

If a certain vector $\boldsymbol{u}$ satisfies Eq. (19.1), any vector collinear with it will also satisfy this equation. Therefore we can speak of the proper directions of a tensor; all vectors parallel to proper directions are the eigenvectors. Direction should be naturally defined by a unit vector. Therefore an auxiliary condition imposed on vector $\mathbf{u}$ will be

$$\boldsymbol{u}\cdot\boldsymbol{u} = u_i u_i = 1. \tag{19.2}$$

Having written Eq. (19.1) in the form

$$(\mathbf{S} - S\mathbf{I})\cdot\boldsymbol{u} = 0, \tag{19.3}$$

$$(S_{ik} - S\delta_{ik})u_k = 0,$$

we see that these are three homogeneous linear equations with unknown components of vector $\boldsymbol{u}$. They are of course satisfied by a trivial solution $\boldsymbol{u} = 0$, but this does not determine a direction. A set of homogeneous linear equations can have, as it is known,

other, non-trivial solutions only when its determinant is zero:

$$\det(\mathbf{S}-S\mathbf{I})=\begin{vmatrix} S_{11}-S & S_{12} & S_{13} \\ S_{21} & S_{22}-S & S_{23} \\ S_{31} & S_{32} & S_{33}-S \end{vmatrix}=0. \qquad (19.4)$$

The tensor S having been given, (19.4) represents an equation which should be satisfied by the eigenvalue of S. Eq. (19.4) is called the *characteristic equation of a tensor*. Insofar as the tensor components are real, this third-degree equation has either one real and two complex-conjugate imaginary roots or three real roots; if the tensor is symmetric, only the latter can be the case. Actually, the equation always has at least one real root $S_{(3)}$. On the assumption of having found it, we can also find the unit vector $u^{(3)}$ corresponding to the eigenvalue $S_{(3)}$ from a set of linear equations

$$(S_{ik}-S_{(3)}\delta_{ik})\,u_k^{(3)}=0.$$

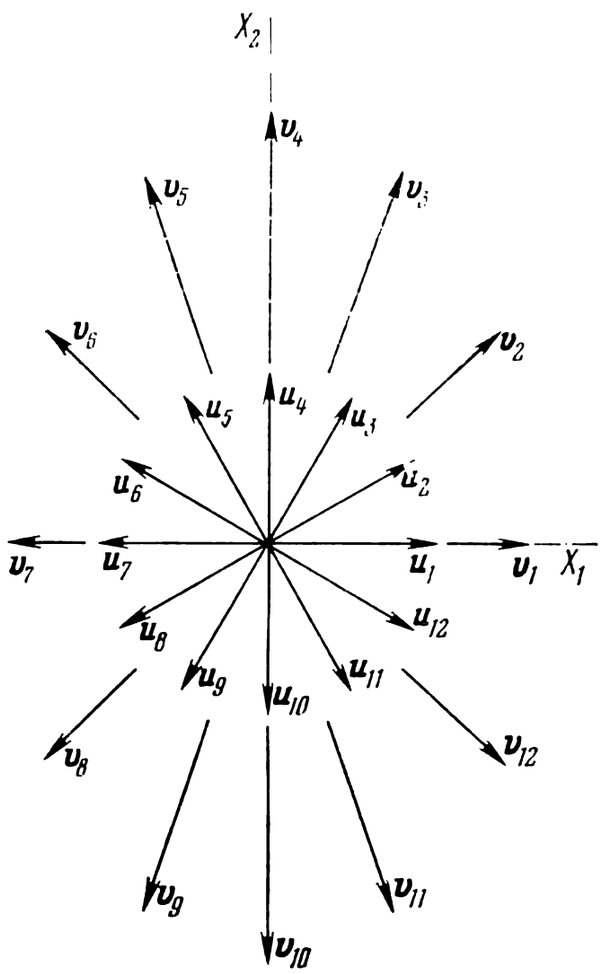


Fig. 19.1. The action of a symmetric tensor S = 3/2 e_1e_1 + 5/2 e_1e_2 on vectors $u_1, \ldots, u_{12}$; $v_i = \mathbf{S}\cdot u_i\cdot u_1$, u_4, u_7 and u_{10} are the eigenvectors of tensor S

Let us introduce the Cartesian coordinates $X_{1'}$, $X_{2'}$, $X_{3'}$, where $u^{(3)}$ serves as the unit vector $e_{3'}$. It can be easily proved that in this set tensor S appears as

$$\| S_{j'l'} \| = \begin{Vmatrix} S_{1'1'} & S_{1'2'} & 0 \\ S_{1'2'} & S_{2'2'} & 0 \\ 0 & 0 & S_{(3)} \end{Vmatrix} \qquad (19.5)$$

(its symmetry having been essentially used). Therefore Eq. (19.4) can be expressed as

$$\begin{vmatrix} S_{1'1'}-S & S_{1'2'} & 0 \\ S_{1'2'} & S_{2'2'}-S & 0 \\ 0 & 0 & S_{(3)}-S \end{vmatrix}=0.$$

Upon the calculation of this determinant we find two other eigenvalues

$$S_{(1,2)} = \frac{1}{2}[(S_{1'1'} + S_{2'2'}) \pm \sqrt{(S_{1'1'} - S_{2'2'})^2 + (2S_{1'2'})^2}]. \qquad (19.6)$$

Insofar as the radicand is positive, as a sum of squares, these two eigenvalues are also real, which completes the proof.

Eigenvectors corresponding to different eigenvalues are mutually orthogonal. Indeed, scalarly multiplying equations for the eigenvectors

$$\mathbf{S} \cdot \boldsymbol{u}^{(1)} = S_{(1)}\boldsymbol{u}^{(1)}, \quad \mathbf{S} \cdot \boldsymbol{u}^{(2)} = S_{(2)}\boldsymbol{u}^{(2)}$$

by $\boldsymbol{u}^{(2)}$ and $\boldsymbol{u}^{(1)}$ respectively, and subtracting one from the other we have

$$\boldsymbol{u}^{(2)} \cdot \mathbf{S} \cdot \boldsymbol{u}^{(1)} - \boldsymbol{u}^{(1)}\mathbf{S} \cdot \boldsymbol{u}^{(2)} = (S_{(1)} - S_{(2)})\, \boldsymbol{u}^{(1)} \cdot \boldsymbol{u}^{(2)}.$$

The left-hand side of this equality is zero because of the symmetry of tensor $\mathbf{S}$, so that the orthogonality of vectors $\boldsymbol{u}^{(1)}$ and $\boldsymbol{u}^{(2)}$ directly follows from the eigenvalues being unequal ($S_{(1)} - S_{(2)} \neq 0$).

If all the eigenvalues of tensor $\mathbf{S}$ are different, its eigenvectors $\boldsymbol{u}^{(k)}$ are mutually orthogonal and can be used as an orthonormalized basis. In this basis the tensor is especially simple:

$$\mathbf{S} = S_{(1)}\boldsymbol{u}^{(1)}\boldsymbol{u}^{(1)} + S_{(2)}\boldsymbol{u}^{(2)}\boldsymbol{u}^{(2)} + S_{(3)}\boldsymbol{u}^{(3)}\boldsymbol{u}^{(3)}, \qquad (19.7)$$

and its matrix takes a diagonal form

$$\| S_{ij} \| = \begin{Vmatrix} S_{(1)} & 0 & 0 \\ 0 & S_{(2)} & 0 \\ 0 & 0 & S_{(3)} \end{Vmatrix}. \qquad (19.8)$$

When two eigenvalues coincide (say, $S_{(1)} = S_{(2)} \neq S_{(3)}$), a whole plane of eigenvectors perpendicular to eigenvector $\boldsymbol{u}^{(3)}$ corresponds to them. Actually, it follows from (19.6) that in any Cartesian system of coordinates where $\boldsymbol{u}^{(3)}$ serves as unit vector $\boldsymbol{e}_3$, tensor $\mathbf{S}$ appears as

$$\begin{Vmatrix} S_{(1)} & 0 & 0 \\ 0 & S_{(1)} & 0 \\ 0 & 0 & S_{(3)} \end{Vmatrix}, \qquad (19.9)$$

this showing that any vector perpendicular to $\boldsymbol{u}^{(3)}$ is the eigenvector of tensor $\mathbf{S}$ corresponding to the eigenvalue $S_{(1)}$. Such tensors can be conveniently written as

$$\mathbf{S} = S_{\perp}\mathbf{I} + (S_{\parallel} - S_{\perp})\, \boldsymbol{kk}, \quad S_{ij} = S_{\perp}\delta_{ij} + (S_{\parallel} - S_{\perp})\, k_i k_j, \qquad (19.10)$$

where $\boldsymbol{k}$ is an isolated (unit) eigenvector, $S_{\parallel}$ is an eigenvalue corresponding to it, and $S_{\perp}$ is an eigenvalue corresponding to the plane of the other eigenvectors.

In case of the coincidence of all the three eigenvalues ($S_{(1)} = S_{(2)} = S_{(3)} = S$), the tensor is

$$\mathbf{S} = S\mathbf{I}, \quad S_{ij} = S\delta_{ij}. \tag{19.11}$$

For this tensor any vector is an eigenvector.

Let us discuss some simple examples of the determinations of eigenvalues and eigenvectors of a symmetric second-rank tensor.

Example 1. In a basis e_k tensor S_{ij} has the form

$$\| S_{ij} \| = \begin{Vmatrix} 11 & \sqrt{3} & 0 \\ \sqrt{3} & 9 & 0 \\ 0 & 0 & 7 \end{Vmatrix}.$$

Let us calculate its eigenvalues by solving the equation

$$\begin{vmatrix} 11-S & \sqrt{3} & 0 \\ \sqrt{3} & 9-S & 0 \\ 0 & 0 & 7-S \end{vmatrix} = 0,$$

or $(S^2 - 20S + 96)(7 - S) = 0$. Hence $S_{(1)} = 12$, $S_{(2)} = 8$, $S_{(3)} = 7$.

An eigenvector $u^{(1)}$ which corresponds to the eigenvalue $S_{(1)} = 12$ will be found from a system of linear equations

$$\begin{aligned} -u_1^{(1)} + \sqrt{3}\, u_2^{(1)} &= 0, \\ \sqrt{3}\, u_1^{(1)} - 3u_2^{(1)} &= 0, \\ -5u_3^{(1)} &= 0. \end{aligned}$$

There are only two independent equations, since the second equation is equal to the first one multiplied by $-\sqrt{3}$. Therefore we find from this set $u_3^{(1)} = 0$, $u_1^{(1)} = \sqrt{3}u_2^{(1)}$. Actually, the first eigenvector has been found: $u^{(1)} = (\sqrt{3}e_1 + e_2)u_2^{(1)}$. Provided that $u^{(1)} \cdot u^{(1)} = 1$, we find that $u_2^{(1)} = \pm 1/2$ and finally obtain

$$u^{(1)} = \pm \left(\frac{\sqrt{3}}{2} e_1 + \frac{1}{2} e_2 \right).$$

The eigenvector $u^{(2)}$ can be found from a system of equations:

$$\begin{aligned} 3u_1^{(2)} + \sqrt{3}u_2^{(2)} &= 0, \\ \sqrt{3}u_1^{(2)} + u_2^{(2)} &= 0, \\ -u_3^{(2)} &= 0. \end{aligned}$$

It is

$$u^{(2)} = \pm \left(\frac{1}{2} e_1 - \frac{\sqrt{3}}{2} e_2 \right).$$

Finally, for the eigenvector $u^{(3)}$ we obtain a set of equations

$$\begin{aligned} 4u_1^{(3)} + \sqrt{3}\, u_2^{(3)} &= 0, \\ \sqrt{3}\, u_1^{(3)} + 2u_2^{(3)} &= 0, \\ 0u_3^{(3)} &= 0. \end{aligned}$$

The first two equations form a system of two homogeneous linear equations in two unknowns. Its determinant equals 5. Therefore it has only a trivial solution $u_1^{(3)} = u_2^{(3)} = 0$. The component $u_3^{(3)}$ can have any value, but from the requirement $\boldsymbol{u}^{(3)} \cdot \boldsymbol{u}^{(3)} = 1$, it follows that $u_3^{(3)} = \pm 1$. So

$$\boldsymbol{u}^{(3)} = \pm \boldsymbol{e}_2.$$

Now tensor S can take the form

$$\mathbf{S} = 12\left(\frac{\sqrt{3}}{2}\boldsymbol{e}_1 + \frac{1}{2}\boldsymbol{e}_2\right)\left(\frac{\sqrt{3}}{2}\boldsymbol{e}_1 + \frac{1}{2}\boldsymbol{e}_2\right) +$$

$$+ 8\left(\frac{1}{2}\boldsymbol{e}_1 - \frac{\sqrt{3}}{2}\boldsymbol{e}_2\right)\left(\frac{1}{2}\boldsymbol{e}_1 - \frac{\sqrt{3}}{2}\boldsymbol{e}_2\right) + 7\boldsymbol{e}_3\boldsymbol{e}_3.$$

Example 2. Let us reduce the tensor

$$\mathbf{S} = 4\,(\boldsymbol{e}_1\boldsymbol{e}_1 + \boldsymbol{e}_2\boldsymbol{e}_2) + 3\boldsymbol{e}_3\boldsymbol{e}_3 - (\boldsymbol{e}_1\boldsymbol{e}_2 + \boldsymbol{e}_2\boldsymbol{e}_1).$$

to the principal axes.

For determining its eigenvalues we use the equation

$$\begin{vmatrix} 4-S & -1 & 0 \\ -1 & 4-S & 0 \\ 0 & 0 & 3-S \end{vmatrix} = 0.$$

Solving it we arrive at $S_{(1)} = 5$, $S_{(2)} = 3$, $S_{(3)} = 3$.

Here it will suffice to find only one eigenvector $\boldsymbol{k}$ which corresponds to $S_{(1)} = 5$. We find it from a set of equations

$$\begin{aligned} -k_1 - k_2 \qquad\qquad &= 0, \\ -k_1 - k_2 \qquad\qquad &= 0, \\ -2k_3 &= 0. \end{aligned}$$

Hence

$$\boldsymbol{k} = \pm\left(\frac{1}{\sqrt{2}}\boldsymbol{e}_1 - \frac{1}{\sqrt{2}}\boldsymbol{e}_2\right),$$

while tensor S takes the form (19.10):

$$\mathbf{S} = 3\mathbf{I} + 2\,\frac{\boldsymbol{e}_1 - \boldsymbol{e}_2}{\sqrt{2}}\,\frac{\boldsymbol{e}_1 - \boldsymbol{e}_2}{\sqrt{2}}.$$

In a general case, for calculating the eigenvalues of tensor S_{ij}, it should be resolved into the spherical part $1/3\, S_{kk}\sigma_{ij}$ and the deviator $D_{ij} = S_{ij} - 1/3\, S_{kk}\delta_{ij}$. Next, two invariants of the deviator are found: the scale parameter being

$$\vartheta = \sqrt{-\frac{1}{6}\delta_{ikm}\,\delta_{jlm}D_{ij}D_{kl}} = \sqrt{\frac{1}{6}D_{ij}D_{ij}} \tag{19.12}$$

and the angle ψ within the limits $(-\pi/6, \pi/6)$ defined by the condition

$$\sin 3\psi = -\frac{\det \mathbf{D}}{2\vartheta^3}. \tag{19.13}$$

The eigenvalues $D_{(i)}$ of the deviator **D** (numbered in the increasing order) are expressed in terms of these invariants thus:

$$\begin{aligned} D_{(1)} &= -2\vartheta \sin(\pi/3+\psi), \\ D_{(2)} &= 2\vartheta \sin\psi, \\ D_{(3)} &= 2\vartheta \sin(\pi/3-\psi). \end{aligned} \tag{19.14}$$

This can be easily verified by substituting any of them in the characteristic equation of the deviator. The eigenvalues of tensor **S** are equal to

$$S_{(i)} = D_{(i)} + \frac{1}{3} S_{kk}. \tag{19.15}$$

Sec. 20. Small Changes of a Symmetric Second-Rank Tensor

The solution of many crystal-physical problems is connected with the following problem of tensor algebra: the eigenvalues $S_{(i)}$ and the eigenvectors* $\boldsymbol{u}_i$ of a symmetric second-rank tensor **S** are known; how will they change under a given small change of tensor **S**?

We shall first discuss a case when all the three eigenvalues of the initial tensor **S** are different. We add a small symmetric tensor ζ to tensor **S**; if the former is small indeed in comparison with β, then the tensor $\mathbf{S} + \zeta$ should differ but little from tensor **S**. The difference will appear, first in small changes of the eigenvalues and, second, in a small rotation of the triplet of eigenvectors $\boldsymbol{u}_1$, $\boldsymbol{u}_2$, $\boldsymbol{u}_3$. For the actual changes $\xi_{(i)}$ of the eigenvalues to be small it is necessary that the absolute values of all the components of tensor ζ be considerably smaller than the eigenvalues of tensor **S**:

$$|\zeta_{kl}| \ll |S_{(i)}|.$$

Also for the rotation of the three eigenvectors to be small the absolute value of tensor ζ components should be considerably smaller than the differences in the eigenvalues of the tensor:

$$|\zeta_{kl}| \ll |S_{(i)} - S_{(j)}|.$$

The changed eigenvalues of $S_{(i)} + \xi_{(i)}$ and the changed eigenvectors $\boldsymbol{u}_i + \delta\boldsymbol{u}_i$ satisfy the equation

$$(\mathbf{S} + \zeta)\cdot(\boldsymbol{u}_i + \delta\boldsymbol{u}_i) = (S_{(i)} + \xi_{(i)})\,(\boldsymbol{u}_i + \delta\boldsymbol{u}_i). \tag{20.1}$$

Without loss of generality, vectors $\boldsymbol{u}_i$ can be considered as unit ones. We shall require the changed vectors $\boldsymbol{u}_i + \delta\boldsymbol{u}_i$ to be also unit ones; besides, we know that they have to be mutually orthogonal:

$$(\boldsymbol{u}_i + \delta\boldsymbol{u}_i)\cdot(\boldsymbol{u}_j + \delta\boldsymbol{u}_j) = \delta_{ij}.$$

Upon opening the brackets, we obtain

$$\boldsymbol{u}_i\cdot\delta\boldsymbol{u}_j + \boldsymbol{u}_j\cdot\delta\boldsymbol{u}_i + \delta\boldsymbol{u}_i\cdot\delta\boldsymbol{u}_j = 0. \tag{20.2}$$

Let us resolve vectors $\delta\boldsymbol{u}_i$ in terms of the basis $\boldsymbol{u}_1$, $\boldsymbol{u}_2$, $\boldsymbol{u}_3$:

$$\delta\boldsymbol{u}_i = \omega_{ik}\boldsymbol{u}_k. \tag{20.3}$$

The coefficients of this expansion are

$$\omega_{ij} = \delta\boldsymbol{u}_i\cdot\boldsymbol{u}_j. \tag{20.4}$$

---

* It is more convenient for further operations to denote the eigenvectors by $\boldsymbol{u}_1$ and not by $\boldsymbol{u}^{(i)}$ as previously.

It follows from (20.2) that tensor ω is antisymmetric, if the terms of the second order of smallness are ignored:

$$\omega_{ji} + \omega_{ij} = 0. \tag{20.5}$$

And hence the increment δu_i of each eigenvector u_i is perpendicular to the vector. Indeed, according to (20.4), the scalar product of the eigenvector and its increment is equal to one of the diagonal components of tensor ω, but due to the identity (20.5) all such components are zero.

Now, let us open the brackets in (20.1), taking for the sake of definiteness $u_i = u_1$ and $S_{(i)} = S_{(1)}$, accordingly

$$\mathbf{S}\cdot u_1 + \mathbf{S}\cdot\delta u_1 + \zeta\cdot u_1 = S_{(1)}u_1 + S_{(1)}\delta u_1 + \xi_1 u_1. \tag{20.6}$$

Here we ignore the infinitesimals of the second order. Assuming that $\mathbf{S}\cdot u_1 = S_{(1)}u_1$ and using expansion (20.4) we rewrite Eq. (20.6) as

$$\omega_{12}\mathbf{S}\cdot u_2 + \omega_{13}\mathbf{S}\cdot u_3 + \zeta\cdot u_1 = \omega_{12}S_{(1)}u_2 + \omega_{13}S_{(1)}u_3 + \xi_{(1)}u_1.$$

However, $\mathbf{S}\cdot u_2 = S_{(2)}u_2$ and $\mathbf{S}\cdot u_3 = S_{(3)}u_3$. Therefore

$$\zeta\cdot u_1 = \xi_{(1)}u_1 + \omega_{12}\,(S_{(1)} - S_{(2)})\,u_2 + \omega_{13}\,(S_{(1)} - S_{(3)})u_3. \tag{20.7}$$

Successive scalar multiplication of both parts of (20.7) by u_1, u_2 and u_3 gives the results sought:

$$\xi_{(1)} = u_1\cdot\zeta\cdot u_1, \quad \omega_{12} = \frac{u_2\cdot\zeta\cdot u_1}{S_{(1)} - S_{(2)}}, \quad \omega_{13} = \frac{u_2\cdot\zeta\cdot u_1}{S_{(1)} - S_{(2)}}. \tag{20.8}$$

The rest of the eigenvalues and tensor ω components are calculated similarly.

If tensor ζ is given by its components ζ_{ij} referred to the principal axes of tensor S, the solution of the problem is obtained as follows:

$$\begin{aligned}
&\xi_{(1)} = \zeta_{11}, && \omega_{23} = -\omega_{32} = \frac{\zeta_{23}}{S_{(2)} - S_{(3)}},\\
&\xi_{(2)} = \zeta_{22}, && \omega_{31} = -\omega_{13} = \frac{\zeta_{31}}{S_{(3)} - S_{(1)}},\\
&\xi_{(3)} = \zeta_{33}, && \omega_{12} = -\omega_{21} = \frac{\zeta_{12}}{S_{(1)} - S_{(2)}}.
\end{aligned} \tag{20.9}$$

The antisymmetric tensor ω characterizes a small rotation of the triplet of eigenvectors. For this rotation to be really small, all the components of tensor ω should be much less than unity, and for this, as shown by Eqs. (20.9), it is necessary that the tensor components be small not only in comparison with the eigenvalues of tensor S, but also in comparison with their differences.

Let us now discuss another case: two eigenvalues ($S_\perp$) of tensor S coincide one with another, while the third one ($S_\parallel$) differs from them. In this case the problem becomes much more complicated. Tensor S now has one eigenvector u corresponding to eigenvalue $S_\parallel$ and a whole eigenplane corresponding to the double eigenvalue $S_\perp$. The changed tensor $\mathbf{S} + \zeta$ has, generally, three eigenvectors; one of them, $v = u + \delta u$, is close to u, while the remaining two are located somewhere in the plane perpendicular to the first vector.

Let q_1, q_2 and v be the unit eigenvectors of tensor $\mathbf{S} + \zeta$ while p_1 and p_2 are the projections of tectors q_1 and q_2 onto the eigenplane of tensor S: then the following is valid:

$$q_1 = p_1 + \omega_{13}u, \quad q_2 = p_2 + \omega_{23}u, \quad v = \omega_{31}p_1 + \omega_{32}p_2 + u. \tag{20.10}$$

The three eigenvectors being orthonormalized, it follows that (within the limits of our degree of accuracy) vectors p_1 and p_2 are unit ones and mutually perpendicular, while tensor ω is antisymmetric.

Let us substitute the expressions for the eigenvectors (20.10) in the equations for eigenvalues and eigenvectors

$$\begin{aligned}(\mathbf{S}+\zeta)\cdot \boldsymbol{q}_1 &= (S_\perp + \xi_{(1)})\boldsymbol{q}_1,\\ (\mathbf{S}+\zeta)\cdot \boldsymbol{q}_2 &= (S_\perp + \xi_{(2)})\,\boldsymbol{q}_2,\\ (\mathbf{S}+\zeta)\cdot \boldsymbol{v} &= (S_{||} + \xi_{(3)})\,\boldsymbol{v}\end{aligned} \tag{20.11}$$

and perform a term-by-term scalar multiplication, ignoring the second-order infinitesimals. Upon collecting similar terms we get

$$\begin{aligned}\zeta\cdot \boldsymbol{p}_1 &= \xi_{(1)}\boldsymbol{p}_1 + (S_{||} - S_\perp)\,\omega_{31}\boldsymbol{u},\\ \zeta\cdot \boldsymbol{p}_2 &= \xi_{(2)}\boldsymbol{p}_2 + (S_{||} - S_\perp)\,\omega_{32}\boldsymbol{u},\\ \zeta\cdot \boldsymbol{u} &= (S_{||} - S_\perp)\,(\omega_{31}\boldsymbol{p}_1 + \omega_{32}\boldsymbol{p}_2) + \xi_{(3)}\boldsymbol{u}.\end{aligned} \tag{20.12}$$

By scalar multiplication of vector equalities (20.12) successively by $\boldsymbol{p}_1$, $\boldsymbol{p}_2$ and $\boldsymbol{u}$, we obtain six relations

$$\boldsymbol{u}\cdot\zeta\cdot\boldsymbol{u} = \xi_{(3)}, \tag{20.13}$$

$$\boldsymbol{p}_1\cdot\zeta\cdot\boldsymbol{p}_1 = \xi_{(1)}, \quad \boldsymbol{p}_2\cdot\zeta\cdot\boldsymbol{p}_2 = \xi_{(2)}, \quad \boldsymbol{p}_1\cdot\zeta\cdot\boldsymbol{p}_2 = 0; \tag{20.14}$$

$$\boldsymbol{u}\cdot\zeta\cdot\boldsymbol{p}_1 = (S_{||} - S_\perp)\,\omega_{31}, \quad \boldsymbol{u}\cdot\zeta\cdot\boldsymbol{p}_2 = (S_{||} - S_\perp)\,\omega_{32}, \tag{20.15}$$

which are combined for convenience into three groups.

The relation (20.13) allows a direct calculation of $\xi_{(3)}$.

Vectors $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ are so far unknown, but (20.14) shows that they are the eigenvectors of a two-dimensional tensor $\zeta_\perp$, i.e. the projections of tensor ζ onto the proper plane of tensor S. Accordingly, ξ_1 and ξ_2 are the eigenvalues of this two-dimensional tensor.

Let tensor ζ be given by the matrix of its components $\| \zeta_{ij} \|$ in the reference frame with mutually orthogonal unit vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{u}$, where $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are arbitrarily situated in the proper plane of tensor S. Then the two-dimensional tensor $\zeta_\perp$ referred to the coordinate axes with mutually orthogonal unit vectors $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ is given by the matrix of its components

$$\| \zeta_{ij}^{\perp} \| = \begin{Vmatrix} \zeta_{11} & \zeta_{12} \\ \zeta_{12} & \zeta_{22} \end{Vmatrix}.$$

Its eigenvalues $\xi_{(1)}$ and $\xi_{(2)}$ are the roots of the quadratic equation

$$\begin{vmatrix} \zeta_{11} - \xi & \zeta_{12} \\ \zeta_{12} & \zeta_{22} - \xi \end{vmatrix} = 0. \tag{20.16}$$

They are equal to

$$\xi_{(1,2)} = \frac{1}{2}\left[(\zeta_{11} + \zeta_{22}) \pm \sqrt{(\zeta_{11} - \zeta_{22})^2 + (2\zeta_{12})^2}\right]. \tag{20.17}$$

Now the eigenvectors of tensor $\zeta_\perp$ can be easily found:

$$\boldsymbol{p}_1 = \frac{\zeta_{12}\boldsymbol{e}_1 + (\xi_{(1)} - \zeta_{11})\boldsymbol{e}_2}{\sqrt{(\xi_{(1)} - \zeta_{11})^2 + \zeta_{12}^2}}, \quad \boldsymbol{p}_2 = \frac{(\xi_{(2)} - \zeta_{22})\,\boldsymbol{e}_1 + \zeta_{12}\boldsymbol{e}_2}{\sqrt{(\xi_{(2)} - \zeta_{22})^2 + \zeta_{12}^2}}. \tag{20.18}$$

The relations (20.14) have been thus fully utilized.

Vectors $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ being known, coefficients ω_{31} and ω_{32} can be found now from (20.15). Apparently

$$\omega_{31}=\frac{\zeta_{12}\zeta_{31}+\zeta_{23}(\xi_{(1)}-\zeta_{11})}{(S_{\parallel}-S_{\perp})\sqrt{(\xi_{(1)}-\zeta_{11})^2+\zeta_{12}^2}},$$
$$\omega_{32}=\frac{\zeta_{12}\zeta_{23}+\zeta_{31}(\xi_{(2)}-\zeta_{22})}{(S_{\parallel}-S_{\perp})\sqrt{(\xi_{(2)}-\zeta_{22})^2+\zeta_{12}^2}}. \tag{20.19}$$

Finally, eigenvectors $\boldsymbol{q}_1$, $\boldsymbol{q}_2$ and $\boldsymbol{v}$ of tensor $\mathbf{S}+\zeta$ can be found with the aid of (20.10). The problem is completely solved.

It is evidently useless to consider the case when all the eigenvalues of tensor $\mathbf{S}$ coincide. The eigenvectors of tensor $\mathbf{S}+\zeta$ coincide in this case with the eigenvectors of tensor ζ, and the corresponding increments to the eigenvalues are equal to the eigenvalues of tensor ζ.

Sec. 21. Normal and Tangential Components of a Second-Rank Symmetric Tensor

A number equal to

$$\boldsymbol{n}\cdot\mathbf{S}\cdot\boldsymbol{n}=S_{ij}n_in_j \tag{21.1}$$

is called the *normal component* of a symmetric second-rank tensor $\mathbf{S}$ in the direction of the unit vector $\boldsymbol{n}$.

If $\boldsymbol{n}$ is taken to be one of the unit vectors of the new coordinate system $X_{1'}$, $X_{2'}$, $X_{3'}$ (let us say, $\boldsymbol{n}=\boldsymbol{e}_{1'}$), then the normal component will be exactly the corresponding diagonal component of the tensor in system $X_{1'}$, $X_{2'}$, $X_{3'}$; in this instance

$$\boldsymbol{n}\cdot\mathbf{S}\cdot\boldsymbol{n}=S_{1'1'}. \tag{21.2}$$

In a system of coordinates constructed on the principal axes of the tensor the formulas for calculating its normal component appear especially simple. Assuming that n_i are the components of the unit vector $\boldsymbol{n}$ with respect to the proper coordinate system of tensor $\mathbf{S}$, we obtain

$$\boldsymbol{n}\cdot\mathbf{S}\cdot\boldsymbol{n}=S_{(1)}n_1^2+S_{(2)}n_2^2+S_{(3)}n_3^2. \tag{21.3}$$

If, in particular, two eigenvalues of tensor $\mathbf{S}$ coincide, its normal component will depend only on $n_3=\boldsymbol{n}\cdot\boldsymbol{k}$:

$$\boldsymbol{n}\cdot\mathbf{S}\cdot\boldsymbol{n}=S_{\perp}(1-n_3^2)+S_{\parallel}n_3^2=S_{\perp}+(S_{\parallel}-S_{\perp})n_3^2.$$

Finally, if all the three eigenvalues of the tensor coincide, the normal component $\boldsymbol{n}\cdot\mathbf{S}\cdot\boldsymbol{n}=S$.

Knowing six normal components of a symmetric second-rank tensor $\mathbf{S}$ it is possible, generally, to calculate all the components of the tensor. They will be the solution of a set of six linear equations in six unknowns

$$n_i^{(\mu)}n_j^{(\mu)}S_{ij}=\alpha_{(\mu)}\quad(\mu=1,\ \ldots,\ 6), \tag{21.4}$$

where the components of unit vector $\boldsymbol{n}^{(\mu)}$ and the corresponding normal components $\alpha_{(\mu)}$ are supposed to be known. The determinant of this set must be non-zero, this being a necessary and sufficient condition for the solution of the system:

$$\begin{vmatrix} (n_1^{(1)})^2 & (n_2^{(1)})^2 & (n_3^{(1)})^2 & 2n_2^{(1)}n_3^{(1)} & 2n_3^{(1)}n_1^{(1)} & 2n_1^{(1)}n_2^{(1)} \\ (n_1^{(2)})^2 & (n_2^{(2)})^2 & (n_3^{(2)})^2 & 2n_2^{(2)}n_3^{(2)} & 2n_3^{(2)}n_1^{(2)} & 2n_1^{(2)}n_2^{(2)} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ (n_1^{(6)})^2 & (n_2^{(6)})^2 & (n_3^{(6)})^2 & 2n_2^{(6)}n_3^{(6)} & 2n_3^{(6)}n_1^{(6)} & 2n_1^{(6)}n_2^{(6)} \end{vmatrix} \neq 0. \qquad (21.5)$$

Obviously not any set of six unit vectors $\boldsymbol{n}^{(\mu)}$ satisfies (21.5), but there is no difficulty in pointing out such sets of vectors which do satisfy it, for example

$$\boldsymbol{n}^{(1)} = \boldsymbol{e}_1, \qquad \boldsymbol{n}^{(2)} = \boldsymbol{e}_2, \qquad \boldsymbol{n}^{(3)} = \boldsymbol{e}_3,$$
$$\boldsymbol{n}^{(4)} = \frac{\boldsymbol{e}_2 + \boldsymbol{e}_3}{\sqrt{2}}, \quad \boldsymbol{n}^{(5)} = \frac{\boldsymbol{e}_3 + \boldsymbol{e}_1}{\sqrt{2}}, \quad \boldsymbol{n}^{(6)} = \frac{\boldsymbol{e}_1 + \boldsymbol{e}_2}{\sqrt{2}}. \qquad (21.6)$$

Normal components often occur in the solutions of crystal-physical problems, therefore of great practical significance is the direction of vector $\boldsymbol{n}$ at which the normal component of a given tensor $\mathbf{S}$ takes its extreme values. What are these values? It is assumed that tensor $\mathbf{S}$ is given by its components S_{ij} referred to a certain coordinate system X_1, X_2, X_3.

Mathematically this problem is formulated thus: the values of n_i should be found at which the quadratic form

$$F(\boldsymbol{n}) = \boldsymbol{n} \cdot \mathbf{S} \cdot \boldsymbol{n} = S_{ij} n_i n_j \qquad (21.7)$$

attains its extremum with the additional condition that

$$f(\boldsymbol{n}) = \boldsymbol{n} \cdot \boldsymbol{n} - 1 = n_i n_i - 1 = 0. \qquad (21.8)$$

This is a typical problem in finding a conditional extremum. Such problems are solved by the Lagrange method of undetermined multipliers: a function

$$\Phi(\boldsymbol{n}) = F(\boldsymbol{n}) - \lambda f(\boldsymbol{n}) \qquad (21.9)$$

with an undetermined factor λ is composed, and its absolute extremum is found by the usual method, i.e. its partial derivatives are equated to zero:

$$\frac{\partial \Phi}{\partial n_i} = 0, \qquad (21.10)$$

then components n_i and factor λ are found from equations (21.10) and (21.8). Equations (21.10) will in our case appear as

$$\frac{\partial \Phi}{\partial n_i} = \frac{\partial F}{\partial n_i} - \lambda \frac{\partial f}{\partial n_i} = S_{ij} n_j + S_{ji} n_j - 2\lambda n_i = 0,$$

or (taking into account that the tensor S is symmetric) as

$$S_{ij}n_j = \lambda n_i, \quad \mathbf{S}\cdot\boldsymbol{n} = \lambda\boldsymbol{n}, \tag{21.11}$$

but this is nothing else but the condition for $\boldsymbol{n}$ to be one of the eigenvectors of tensor S and λ to be the eigenvalue corresponding to this vector!

Thus the tensor's normal component attains its extreme values in the directions of its eigenvectors. Moreover, these extreme values are equal to the corresponding eigenvalues of the tensor, since it follows from (21.11) and (21.8) that

$$\boldsymbol{n}\cdot\mathbf{S}\cdot\boldsymbol{n} = S_{ij}n_in_j = \lambda n_in_i = \lambda. \tag{21.12}$$

It also follows from the above proofs that if all the eigenvalues of a tensor are positive (negative), then all its normal components have the same property. Should the tensor's eigenvalues be both positive and negative, its normal component also takes on both positive and negative values. Since it is a continuous function of direction, the component should become zero inside a certain cone of directions.

Let us now consider the tangential components of a second-rank symmetric tensor. Let S be a symmetric second-rank tensor, and $\boldsymbol{p}$ and $\boldsymbol{q}$ be mutually perpendicular unit vectors

$$\boldsymbol{p}\cdot\boldsymbol{p} = 1, \quad \boldsymbol{q}\cdot\boldsymbol{q} = 1, \quad \boldsymbol{p}\cdot\boldsymbol{q} = 0. \tag{21.13}$$

A *tangential component* of tensor S in directions $\boldsymbol{p}$ and $\boldsymbol{q}$ is the quantity

$$\boldsymbol{p}\cdot\mathbf{S}\cdot\boldsymbol{q} = S_{ij}p_iq_j. \tag{21.14}$$

Since tensor S is symmetric, directions $\boldsymbol{p}$ and $\boldsymbol{q}$ in this definition possess equal rights and are interchangeable. Unit vectors $\boldsymbol{p}$ and $\boldsymbol{q}$ being mutually perpendicular, it is possible to use them for constructing a new system of coordinates $X_{1'}$, $X_{2'}$, $X_{3'}$:

$$\boldsymbol{e}_{1'} = \boldsymbol{p}, \quad \boldsymbol{e}_{2'} = \boldsymbol{q}, \quad \boldsymbol{e}_{3'} = \boldsymbol{p}\times\boldsymbol{q}.$$

In the new system the tangential component is

$$\boldsymbol{p}\cdot\mathbf{S}\cdot\boldsymbol{q} = S_{1'2'}. \tag{21.15}$$

While the normal components correspond to the diagonal components of the tensor, the tangential ones correspond to the non-diagonal ones.

In a proper system of coordinates the tangential components are expressed as follows: in a general case

$$\boldsymbol{p}\cdot\mathbf{S}\cdot\boldsymbol{q} = S_{(1)}p_1q_1 + S_{(2)}p_2q_2 = S_{(3)}p_3q_3, \tag{21.16}$$

in case of a coincidence of two eigenvalues

$$\boldsymbol{p}\cdot\mathbf{S}\cdot\boldsymbol{q} = (S_{\parallel} - S_{\perp})\,p_3q_3, \tag{21.17}$$

and, finally, in case of a coincidence of all the three eigenvalues

$$\boldsymbol{p}\cdot\mathbf{S}\cdot\boldsymbol{q} = 0. \tag{21.18}$$

Since the tangential components of a spherical tensor are zero, it is evident that the tangential components of any tensor coincide with the tangential components of its deviator. Accordingly, not the whole tensor but at best its deviator can be reconstructed given a set of its tangential components. Five tangential components will suffice for the purpose.

The extremal problem is much more complicated for the tangential components than for the normal ones, but it is solved in the same way. Suppose values of p_i and q_i should be found at which the bilinear form

$$F(\boldsymbol{p}, \boldsymbol{q}) = S_{ij}p_iq_j \tag{21.19}$$

attains its extremum and which satisfy additional conditions

$$\varphi(\boldsymbol{p}) = p_ip_i - 1 = 0, \quad \varphi(\boldsymbol{q}) = q_iq_i - 1 = 0, \quad \psi(\boldsymbol{p}, \boldsymbol{q}) = p_iq_i = 0. \tag{21.20}$$

Let us compose a function

$$\Phi(\boldsymbol{p}, \boldsymbol{q}) = F(\boldsymbol{p}, \boldsymbol{q}) - \frac{1}{2}\lambda'\varphi(\boldsymbol{p}) - \frac{1}{2}\lambda''\varphi(\boldsymbol{q}) - \mu\psi(\boldsymbol{p}, \boldsymbol{q}) \tag{21.21}$$

where λ', λ'' and μ are Lagrange's undetermined multipliers. From equations

$$\frac{\partial\Phi}{\partial p_i} = 0, \quad \frac{\partial\Phi}{\partial q_i} = 0 \tag{21.22}$$

and (21.20) we find the required vectors $\boldsymbol{p}$ and $\boldsymbol{q}$ as well as the values of Lagrange's multipliers. Equations (21.22), with tensor S being symmetric, give

$$\begin{aligned} S_{ij}q_j - \lambda' p_i - \mu q_i = 0, \\ S_{ij}p_j - \lambda'' q_i - \mu p_i = 0. \end{aligned} \tag{21.23}$$

In a vector form these six equations come to two equations:

$$\begin{aligned} \mathbf{S}\cdot\boldsymbol{q} - \lambda'\boldsymbol{p} - \mu\boldsymbol{q} = 0, \\ \mathbf{S}\cdot\boldsymbol{p} - \lambda''\boldsymbol{q} - \mu\boldsymbol{p} = 0. \end{aligned} \tag{21.24}$$

By a scalar multiplication of the first of them by $\boldsymbol{q}$ and of the second one by $\boldsymbol{p}$, we find

$$\mu = \boldsymbol{q}\cdot\mathbf{S}\cdot\boldsymbol{q} = \boldsymbol{p}\cdot\mathbf{S}\cdot\boldsymbol{p}; \tag{21.25}$$

conversely, a scalar multiplication of the first equation (21.24) by $\boldsymbol{p}$ and the second one by $\boldsymbol{q}$ gives

$$\lambda' = \lambda'' = \boldsymbol{p}\cdot\mathbf{S}\cdot\boldsymbol{q}; \tag{21.26}$$

we shall denote this value simply by λ. Having done this, we shall add vector equations (21.24) one to the other and subtract them one from the other; in order to deal with unit vectors, as before, we divide both the sum and the difference by $\sqrt{2}$. The following vector equations will result

$$\begin{aligned} \mathbf{S}\cdot\frac{\boldsymbol{q}+\boldsymbol{p}}{\sqrt{2}} - (\mu + \lambda)\frac{\boldsymbol{q}+\boldsymbol{p}}{\sqrt{2}} = 0, \\ \mathbf{S}\cdot\frac{\boldsymbol{q}-\boldsymbol{p}}{\sqrt{2}} - (\mu - \lambda)\frac{\boldsymbol{q}-\boldsymbol{p}}{\sqrt{2}} = 0, \end{aligned} \tag{21.27}$$

They show that $(q+p)/\sqrt{2}$ and $(q-p)/\sqrt{2}$ are the eigenvectors of tensor S, while $\mu+\lambda$ and $\mu-\lambda$ are the eigenvalues corresponding to them.

Let, for instance,

$$\frac{q+p}{\sqrt{2}}=u^{(1)}, \qquad \frac{q-p}{\sqrt{2}}=u^{(2)},$$

then $\mu+\lambda=S_{(1)}$, $\mu-\lambda=S_{(2)}$. Hence we find

$$q=\frac{u^{(1)}+u^{(2)}}{\sqrt{2}}, \qquad p=\frac{u^{(1)}-u^{(2)}}{\sqrt{2}},$$

$$\lambda=\frac{S_{(1)}-S_{(2)}}{2}, \qquad \mu=\frac{S_{(1)}+S_{(2)}}{2};$$

by exchanging the roles of vectors $u^{(1)}$ and $u^{(2)}$, we obtain

$$\lambda=\frac{S_{(2)}-S_{(1)}}{2}.$$

Evidently, the maximum value of function $F(p, q)=p\cdot S\cdot q=S_{ij}p_iq_i$ is equal to half the difference between the maximum and the minimum eigenvalue of tensor S, while the minimum value of this function is equal to the same half difference with an opposite sign. The directions p and q at which function F attains its extreme values are bisectrices of angles between eigenvectors corresponding to maximum and minimum eigenvalues.

Sec. 22. External Symmetry and Representation of Vectors and Second-Rank Symmetric Tensors

If under some transformation of coordinates all the tensor components remain unchanged, the tensor is said to be *invariant* with respect to this transformation. The set of orthogonal transformations, with respect to which a certain tensor is invariant, forms this tensor's *group of external symmetry*. Let us consider the external symmetry of vectors and symmetric second-rank tensors (Shubnikov, 1949).

Representation of a vector by an arrow implies that its symmetry group is the Curie limit group ∞m, the axis of symmetry coinciding with the vector direction. To prove this, we shall choose the old system of coordinates so that the X_3 axis is in the direction of our vector v. This means that $v_1=v_2=0$, $v_3=v$ or $v_k=v\delta_{k3}$. Hence vector v components in any new coordinate system would be equal to $v_{i'}=c_{i'3}v$. For the equality $v_{i'}=v\delta_{i'3}$ to be valid in the new system too, it is necessary that $c_{i'3}=\delta_{i'3}$. It can be easily shown that all orthogonal matrices satisfying this condition can be presented in one of the two forms:

$$\begin{Vmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \quad \begin{Vmatrix} -\cos 2\psi & -\sin 2\psi & 0 \\ -\sin 2\psi & \cos 2\psi & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \quad \begin{matrix} 0\leqslant\varphi<2\pi, \\ 0\leqslant\psi<\pi. \end{matrix} \qquad (22.1)$$

It can be seen from Table 17.1 that these are the matrices of the ∞m group and that the ∞ axis coincides with X_3, i.e. with vector r.

In discussing the second-rank tensor symmetry it is necessary to distinguish three cases, in accordance with the number of coincident eigenvalues of the given tensor. If all of its eigenvalues coincide among themselves, i.e. $\mathbf{S} = S\mathbf{I}$, the tensor is invariant with respect to any orthogonal transformation. Its group of symmetry is $\infty\infty m$ and it is called an *isotropic* or *spherical* tensor.

In case of the coincidence of its two eigenvalues, tensor $\mathbf{S} = S_{\perp}\mathbf{I} + (S_{\parallel} - S_{\perp})\,\boldsymbol{kk}$ (for the explanation of this notation see Sec. 18, p. 144). Let us choose the old system of coordinates so that axis X_3 coincides with the direction $\boldsymbol{k}$. We shall discuss only the second term, since the first one is known to be invariant with respect to any orthogonal transformation. In the old coordinate system the only component of the second term different from zero is $S_{33}^{(2)} = S_{\parallel} - S_{\perp}$. Therefore in any new coordinate system its components would equal $S_{i'j'}^{(2)} = c_{i'3}c_{j'3}S_{33}^{(2)}$. For the components in the new system to be the same as in the old one it is necessary that $c_{i'3} = \pm\delta_{i'3}$. All the orthogonal matrices satisfying this requirement can be presented in one of the forms of (22.1) in case $c_{i'3} = \delta_{i'3}$, and, for $c_{i'3} = -\delta_{i'3}$, in one of the following forms:

$$\begin{Vmatrix} -\cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & -\cos\varphi & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \quad \begin{Vmatrix} \cos 2\psi & \sin 2\psi & 0 \\ \sin 2\psi & -\cos 2\psi & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \quad \begin{matrix} 0 \leqslant \varphi < 2\pi \\ 0 \leqslant \psi < \pi. \end{matrix} \tag{22.2}$$

The matrices of the four listed types (22.1), (22.2) together form the ∞/mm group, as can be seen from Table 17.1. The axis ∞ of this group has the direction of its eigenvector $\boldsymbol{k}$. Tensors of this symmetry are called *transverselyisotropic*.

In case all the three tensor eigenvalues are different, we choose its proper system of coordinates as the old system. Only three components of the system differ from zero: $S_{11} = S_{(1)}$, $S_{22} = S_{(2)}$, and $S_{33} = S_{(3)}$. Obviously all the tensor components in the new coordinate system will remain unchanged, if the matrix of orthogonal transformation is

$$c_{i'k} = \begin{Vmatrix} \pm 1 & 0 & 0 \\ 0 & \pm 1 & 0 \\ 0 & 0 & \pm 1 \end{Vmatrix}. \tag{22.3}$$

This requirement is satisfied by eight matrices of the *mmm* group. Two-fold axes of this group have the direction of the eigenvectors of the tensor $\mathbf{S}$.

The external symmetry of tensors and vectors is lucid, when they are shown graphically. So as to show the symmetric tensors of the second rank characteristic and representation surfaces are used.

The representation surface of tensor **S** is specified by equation

$$r(\boldsymbol{n}) = \boldsymbol{n}\cdot\mathbf{S}\cdot\boldsymbol{n} = S_{ij}n_i n_j, \tag{22.4}$$

which means that in each direction $\boldsymbol{n}$ from the origin there are drawn segments equal in length to the normal component of tensor **S** in this same direction; the ends of these segments form a representation surface. Since six duly chosen normal components of a symmetric second-rank tensor fully define it, it is evident that the whole tensor can be all the more restored with the aid of its representation surface.

Expressing the components of a unit vector $\boldsymbol{n}$ in spherical coordinates (Fig. 22.1)

$$n_1 = \sin\vartheta\cos\varphi, \quad n_2 = \sin\vartheta\sin\varphi, \quad n_3 = \cos\vartheta, \tag{22.5}$$

we obtain the equation of the representation surface in these coordinates. It will be of the simplest form if the unit vectors from which angles ϑ and φ are read off, coincide with the tensor eigenvectors. If all the tensor's eigenvalues are different, then

$$r = (S_{(1)}\cos^2\varphi + S_{(2)}\sin^2\varphi)\sin^2\vartheta + S_{(3)}\cos^2\vartheta. \tag{22.6}$$

If two of its eigenvalues coincide, then

$$r = S_{\perp} + (S_{\parallel} - S_{\perp})\cos^2\vartheta; \tag{22.7}$$

the independence of r from angle φ shows that this is a surface of revolution whose axis coincides with the eigenvector. Finally, the representation surface for tensor $\mathbf{S} = S\mathbf{I}$ is a sphere $r = S$.

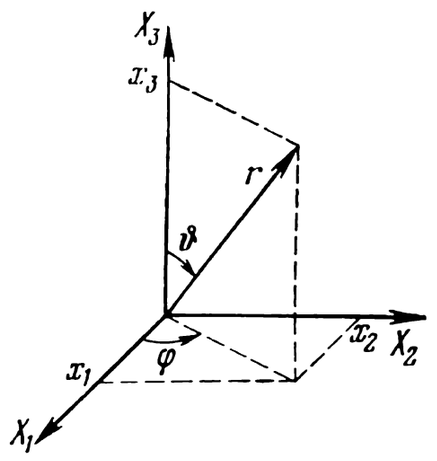


Fig. 22.1. On the relation between spherical (r, ϑ, φ) and Cartesian (x_1, x_2, x_3) coordinates

If all the eigenvalues of tensor **S** are positive, the distance r of any point of the representation surface from the origin will also be positive. But if there occur negative eigenvalues, then r will also be negative for some directions. Since the distance between any two points is a non-negative number, the corresponding surface cannot be constructed with the aid of ordinary geometry. A. V. Shubnikov suggested that in such cases the parts of a representation surface corresponding to negative values of r should be constructed just as ordinary positive parts of the surface, but in distinction from the latter, the former should be coloured black.

Fig. 22.2 shows different types of representation surfaces. The symmetry of these surfaces depends only on the number of different eigenvalues of the tensor, but not on the sign of their eigenvalues, nor on which of the values is greater. Fig. 22.2 confirms that in

case of three different eigenvalues the symmetry of the representation surface is *mmm*; the 2-fold axes coincide with the tensor's eigenvectors. If the tensor has two coincident eigenvalues, the symmetry of the representation surface is ∞/mm; the axis of the infinite order coincides with the eigenvector, the plane of symmetry perpendicular to

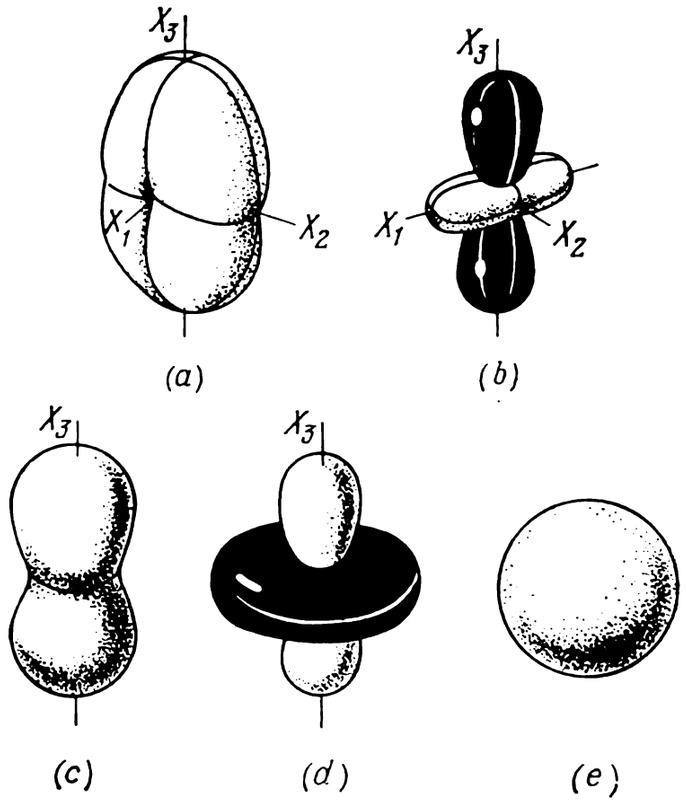


Fig. 22.2. Representation surfaces of symmetric second-rank tensors S. Tensors of the *mmm* symmetry: (a) when $S_{(3)} > S_{(2)} > S_{(1)} > 0$; (b) when $S_{(1)} > S_{(2)} > 0 > S_{(3)}$. Tensors of the ∞/mm symmetry; (c) when $S_{\parallel} > S_{\perp} > 0$; (d) when $S_{\parallel} > 0 > S_{\perp}$; (e) Tensor of the $\infty/\infty m$ symmetry when $S > 0$. Coordinate axes are directed along eigenvectors

it coincides with the plane of the eigenvectors. And, finally, if the tensor has only one eigenvalue, the symmetry of the representation surface is $\infty/\infty m$.

A representation surface can be also constructed for a vector. The normal component of vector $\boldsymbol{v}$ in the direction of the unit vector $\boldsymbol{n}$ is $\boldsymbol{v}\cdot\boldsymbol{n}$, a natural definition. The representation surface of vector $\boldsymbol{v}$ is specified by equation

$$r(\boldsymbol{n}) = \boldsymbol{v}\cdot\boldsymbol{n} = v_i n_i. \tag{22.8}$$

In optional choice of the axes from which angles ϑ and φ are counted off, the equation appears rather complicated

$$r = (v_1 \cos\varphi + v_2 \sin\varphi)\sin\vartheta + v_3 \cos\vartheta,$$

but if the positive direction of axis X_3, from which angle ϑ is counted off, is brought into coincidence with vector $\boldsymbol{v}$, then (22.8) ap-

pears as

$$r = v \cos \vartheta. \tag{22.9}$$

Since angle φ is not included in (22.9), it is the equation of a surface of revolution. The surface represents two contacting spheres—a white and a black one (Fig. 22.3), the diameter of each being v. The symmetry group ∞m of this figure coincides, as was to be expected, with the external symmetry group of the vector.

For showing a symmetric second-rank tensor **S** an *indicatrix* (or a *characteristic surface*) is also used. This is a surface of the second degree defined by the equation

$$\boldsymbol{r}\cdot\mathbf{S}\cdot\boldsymbol{r} = 1, \quad S_{ij}x_ix_j = 1. \tag{22.10}$$

In a system of coordinates constructed on the principal axes of the tensor (22.10) takes the form

$$S_{(1)}x_1^2 + S_{(2)}x_2^2 + S_{(3)}x_3^2 = 1 \tag{22.11}$$

and, depending on the signs of the eigenvalues, specifies an ellipsoid (+++), a one-sheet hyperboloid (++−), a two-sheet hyperboloid (+−−) or an imaginary ellipsoid (−−−).

Representing the radius-vector $\boldsymbol{r}$ as $\boldsymbol{r} = r\boldsymbol{p}$, where r is its length and $\boldsymbol{p}$ is a unit vector, we find from (22.10) that

$$r = \frac{1}{\sqrt{\boldsymbol{p}\cdot\mathbf{S}\cdot\boldsymbol{p}}} = \frac{1}{\sqrt{S_{ik}p_ip_k}}. \tag{22.12}$$

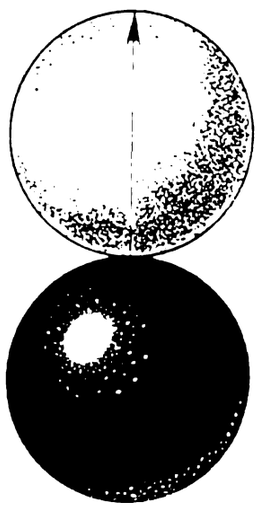


Fig. 22.3. Representation surface of a vector: the group of surface symmetry is ∞m, the antisymmetry group (see Sec. 68) is $\infty/m'm$

Thus the indicatrix is situated within those cones in which the white parts of the representation surface are located, the radius-vector of the indicatrix being inversely proportional to the square root of the radius-vector of the representation surface in the same direction.

In other words, the distance of any point of the indicatrix from its centre is the reciprocal of the square root of the normal component in the direction corresponding to the given point. This conclusion, as well as (22.12) itself, has sense only when all the eigenvalues of the tensor are positive. In practice the indicatrices are ordinarily used for tensors whose eigenvalues are all positive. They are especially widely used in crystal optics, see the optical indicatrix, Fresnel's ellipsoid in Secs. 35, 36. Amongst all possible central sections of an ellipsoid, i.e. sections through its centre, there are distinguished circular sections—central sections that have the shape of a circumference. The directions perpendicular to circular sections of an indicatrix in crystal optics are called optic axes. Apparently, any central section of a sphere is circular, and any of its diameters is an optic

axis. The circular section of an ellipsoid of revolution is its section by the plane of eigenvectors, and the ellipsoid's optic axis is the axis of symmetry of an infinite order. Therefore a symmetric second-rank tensor with two coincident eigenvalues is called not only a transversely isotropic one but also uniaxial.

A general ellipsoid has two circular sections and, accordingly, two optic axes. Therefore a symmetric second-rank tensor with three different eigenvalues is sometimes called biaxial.

Every symmetric second-rank tensor has *isotropic planes*; the central sections of the tensor indicatrix and representation surface by these planes are circumferences. We shall call the perpendicular to the isotropic planes the *axes of isotropy*. Apparently any central section of an isotropic tensor is an isotropic plane, and any direction is an axis of isotropy. The isotropic plane of a transversely isotropic tensor is the plane of its eigenvectors. Since a transversely isotropic tensor has only one isotropy axis, it is also called *uniaxial* (F. I. Fedorov, 1958, 1965).

A tensor with three different eigenvalues has two isotropy axes, because surfaces of the second degree

$$S_{(1)}x_1^2 + S_{(2)}x_2^2 + S_{(3)}x_3^2 = 1,$$

where $S_{(1)} \neq S_{(2)} \neq S_{(3)}$, have two circular sections. Therefore such tensors are called biaxial. Actually, any pair of unit vectors c' and c'' can be connected with tensors

$$\mathbf{S} = a\mathbf{I} + b(\boldsymbol{c}'\boldsymbol{c}'' + \boldsymbol{c}''\boldsymbol{c}'), \quad S_{ij} = a\delta_{ij} + b(c'_i c''_j + c''_i c'_j). \tag{22.13}$$

On the assumption that c' and c'' are the unit vectors of optic axes, (22.13) is called the *optical representation of a tensor*. All the normal components of tensor $\mathbf{S}$ in the directions perpendicular to any of the vectors c' and c'' are equal between themselves: both for $\boldsymbol{n}\cdot\boldsymbol{c}' = 0$ as well as for $\boldsymbol{n}\cdot\boldsymbol{c}'' = 0$,

$$\boldsymbol{n}\cdot\mathbf{S}\cdot\boldsymbol{n} = a\boldsymbol{n}\cdot\mathbf{I}\cdot\boldsymbol{n} + b\,(\boldsymbol{n}\cdot\boldsymbol{c}'\boldsymbol{c}''\cdot\boldsymbol{n} + \boldsymbol{n}\cdot\boldsymbol{c}''\boldsymbol{c}'\cdot\boldsymbol{n}) = a.$$

This means that the planes perpendicular to vectors c' and c'' are isotropic planes, while the vectors themselves are directed along the isotropy axes. It can be easily verified that the eigenvectors (not normalized!) and the corresponding eigenvalues of tensor $\mathbf{S}$ are equal respectively to

$$\begin{aligned} \boldsymbol{u}^{(1)} &= \boldsymbol{c}' - \boldsymbol{c}'', & S_{(1)} &= a - b(1 - \boldsymbol{c}'\cdot\boldsymbol{c}''); \\ \boldsymbol{u}^{(2)} &= \boldsymbol{c}' \times \boldsymbol{c}'', & S_{(2)} &= a; \\ \boldsymbol{u}^{(3)} &= \boldsymbol{c}' + \boldsymbol{c}'', & S_{(3)} &= a + b(1 + \boldsymbol{c}'\cdot\boldsymbol{c}''). \end{aligned} \tag{22.14}$$

Thus an eigenvector corresponding to an eigenvalue of mean magnitude is perpendicular to the plane of the isotropy axes (i.e. it is directed along the line of intersection of isotropic

planes); the other two eigenvectors are directed along the bisectrices of the angles between isotropy axes. The unit vectors of these axes can be expressed by unit eigenvectors $\boldsymbol{u}^{(i)}$ and the eigenvalues $S_{(1)} < S_{(2)} < S_{(3)}$ of tensor **S**:

$$\boldsymbol{c}' = k_1\boldsymbol{u}^{(1)} + k_3\boldsymbol{u}^{(3)}, \qquad \boldsymbol{c}'' = -k_1\boldsymbol{u}^{(1)} + k_3\boldsymbol{u}^{(3)},$$

$$k_3 = \sqrt{\frac{S_{(3)} - S_{(2)}}{S_{(3)} - S_{(1)}}}, \qquad k_1 \quad \sqrt{\frac{S_{(2)} - S_{(1)}}{S_{(3)} - S_{(1)}}}. \tag{22.15}$$

The isotropy axes of indicatrices used in crystal optics—the optical indicatrix and the Fresnel ellipsoid—are called the *optic axes* of the first and second kind, or *binormals* and *biradials* (see Secs 35, 36). Generally, the representation of tensors in the form of (22.13) is used mainly in crystal optics (F. I. Fedorov, 1958).

Sec. 23. Axial Vectors

In physics besides vectors specifying shift, velocity, acceleration, and force which are quite rationally depicted by an arrow, there are also used vectors of quite another type that specify rotation, angular velocity, angular acceleration, moment of force, a magnetic field strength or induction. They specify rotation about a certain axis and are naturally depicted by a segment parallel to the axis, with the indication of the direction of rotation (direction of circuit) about the axis (Fig. 23.1). The length of the segment should be proportional to the length of the vector. Such vectors are called *axial*; ordinary vectors, in order to distinguish them from axial ones, are sometimes called *polar*.

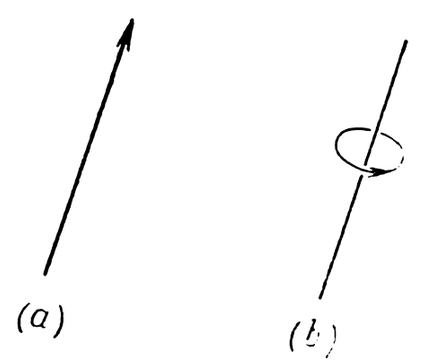


Fig. 23.1. Polar (a) and axial (b) vectors

Axial vectors differ from polar ones by their group of symmetry. The symmetry group of an axial vector is ∞/m. As distinct from the ∞m symmetry group of a polar vector, it is centrosymmetric: an axial vector is invariant with respect to inversion (as well as with respect to reflection in a plane perpendicular to it).

Two intersecting axial vectors form two angles between themselves which supplement each other up to π. If one of the vectors is rotated through one of these angles until it coincides with the second one, then their circuit directions will either coincide with or be opposite to one another. It is the first of these angles that we shall call the angle between axial vectors (Fig. 23.2).

Let us consider the algebra of axial vectors. The multiplication of an axial vector by a positive number λ will increase its length λ

times, but if λ is negative the direction of rotation is at the same time reversed.

The sum of two axial vectors $\mathring{a}$ and $\mathring{b}$ is found similarly to the sum of polar vectors. Here also any of the two equivalent methods can be used: the parallelogram method or the triangle method. According to the first one, a parallelogram is constructed on vectors $\mathring{a}$ and $\mathring{b}$; vector $\mathring{c} = \mathring{a} + \mathring{b}$ coincides with that of the parallelogram diagonals

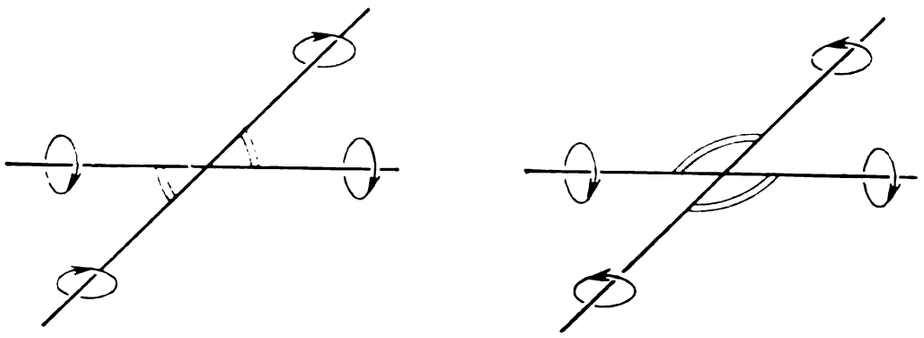


Fig. 23.2. Angles between axial vectors

which cuts the angle between vectors $\mathring{a}$ and $\mathring{b}$, while the by-pass direction is chosen so that when vector $\mathring{c}$ is rotated within the limits of the angle between vectors $\mathring{a}$ and $\mathring{b}$ and coincides with one of these vectors, the by-pass directions coincide (Fig. 23.3).

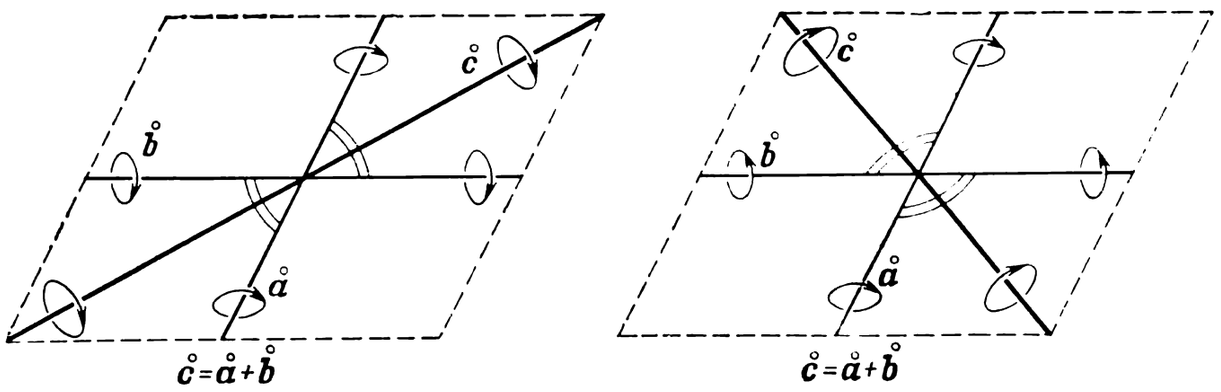


Fig. 23.3. Addition of axial vectors: the parallelogram method

When two axial vectors are added by the triangle method, the ends of vectors $\mathring{a}$ and $\mathring{b}$ are superposed so that the by-pass direction along the resulting broken line does not change. Connecting the free ends by a segment and giving on it the opposite by-pass direction we obtain vector $\mathring{c} = \mathring{a} + \mathring{b}$. As in the case of the composition of polar vectors, this method is easily generalized into the polygon method which allows adding several vectors at once (Fig. 23.4).

The scalar product of two axial vectors is equal to the product of the lengths of these vectors by the cosine of the angle between them: $\mathring{a}\cdot\mathring{b} = ab\cos\gamma$. Scalar multiplication allows introducing an ortho-

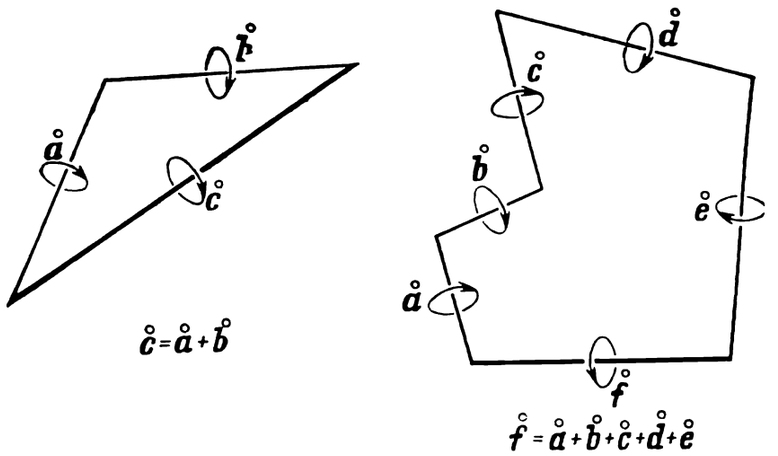


Fig. 23.4. Addition of axial vectors: the triangle (polygon) method

normalized basis $\mathring{e}_1$, $\mathring{e}_2$, $\mathring{e}_3$ consisting of axial vectors ($\mathring{e}_i\cdot\mathring{e}_j = \delta_{ij}$). Any axial vector $\mathring{a}$ can be resolved into this basis:

$$\mathring{a} = \mathring{a}_i\,\mathring{e}_i \tag{23.1}$$

where

$$\mathring{a}_i = \mathring{a}\cdot\mathring{e}_i. \tag{23.2}$$

It can be easily shown that if $\mathring{c} = \mathring{a} + \mathring{b}$, then $\mathring{c}_i = \mathring{a}_i + \mathring{b}_i$ and $\mathring{a}\cdot\mathring{b} = \mathring{a}_i\mathring{b}_i$.

The transformation law for the expansion coefficients $\mathring{a}_i$ is similar to that for the components of a polar vector:
if

$$\mathring{e}_{i'} = \mathring{c}_{i'k}\mathring{e}_k, \tag{23.3}$$

then

$$\mathring{a}_{i'} = \mathring{c}_{i'k}\mathring{a}_k. \tag{23.4}$$

The elements of matrix $\|\mathring{c}_{i'k}\|$ are the cosines of angles between base axial vectors $\mathring{e}_{i'}$ and $\mathring{e}_k$. Since an axial basis is invariant with respect to inversion, it makes no difference whether it is subject to proper rotation $R(\mathring{k}, \varphi)$ by angle φ about a unit vector $\mathring{k}$ or to an inversion rotation $\bar{I}R(\mathring{k}, \varphi)$, matrix $\|\mathring{c}_{i'k}\|$ will just the same coincide with the matrix of a corresponding proper rotation. Therefore under any orthogonal transformation $\det\|\mathring{c}_{i'k}\| = 1$.

True enough, there can be imagined such transformation of an axial vector basis to which will correspond matrices $\|\mathring{c}_{i'k}\|$ with

the determinant —1. Such, for instance, is the transformation of configuration a into configuration b in Fig. 23.5; it is specified by matrix $\| \mathring{c}_{i'k} \| = -\delta_{i'k}$. Such transformations, however, are not orthogonal; they will be discussed in Sec. 71. Within the group of orthogonal transformations the orthonormalized axial vector bases are divided into two classes. Two bases belonging to the same class are made coincident by two orthogonal transformations: $R(\mathring{k}, \varphi)$ and $\bar{1}R(\mathring{k}, \varphi)$ to which corresponds the same matrix $\| \mathring{c}_{i'k} \|$ with

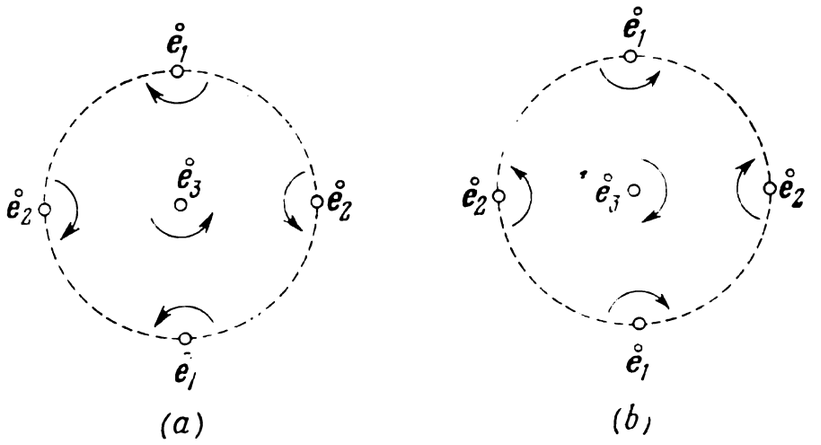


Fig. 23.5. Transformation of an axial vector basis with determinant —1 (stereogram). Basis b cannot be obtained from basis a by any orthogonal transformation

the determinant +1. Bases belonging to different classes cannot be made coincident by any orthogonal transformations whatever, their mutually orthogonal unit vectors make up angles between themselves such that $\det \| \mathring{c}_{i'k} \| = -1$*.

In most physical problems axial vectors are used together with the polar ones, and it is desirable to refer the two types of vectors to the same basis. Only a polar basis is suitable for the purpose, since it changes essentially at each orthogonal transformation, as distinct from an axial basis which is invariant with respect to inversion.

Let us take an arbitrary orthonormalized polar vector basis e_1, e_2, e_3. Let us construct on it an axial basis $\mathring{e}_1, \mathring{e}_2, \mathring{e}_3$ so that $\mathring{e}_1$ coincides with e_1, $\mathring{e}_2$ with e_2 and $\mathring{e}_3$ with e_3. The by-pass directions about axial base vectors we determine according to the numeration of polar vectors: the by-pass direction about $\mathring{e}_1$ is chosen from the end of

* Should there be discussed not only the orthogonal but all homogeneous linear transformations, the axial vector bases (which of course would not be orthonormalized) would also be of two classes, so that no such transformation would make two bases of different classes coincide.

vector e_2 to the end of e_3, the by-pass direction about $\overset{\circ}{e}_2$ is from the end of e_3 to the end of e_1, and about $\overset{\bullet}{e}_3$ it is from the end of e_1 to the end of e_2 (Fig. 23.6). This determination of the by-pass direction is invariant: it remains unchanged in any orthogonal transformations whatever; to verify this, it will suffice to subject the obtained figure

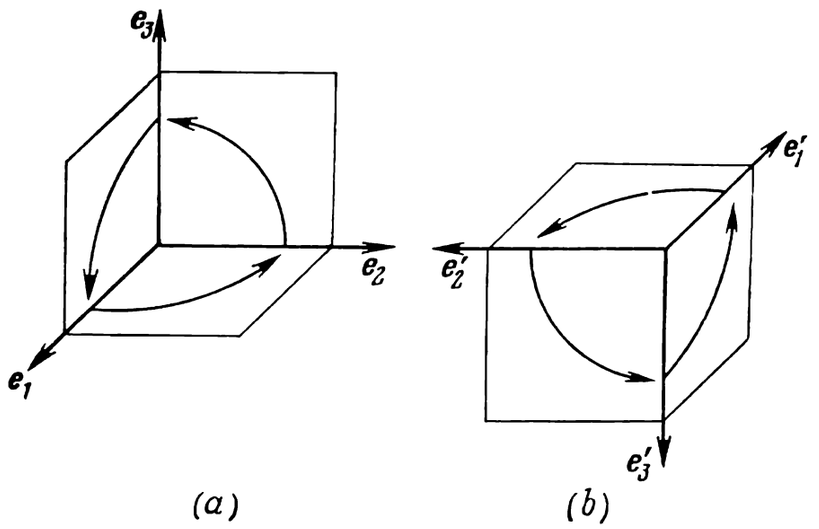


Fig. 23.6. Determination of by-pass directions about base vectors (a) and their retention under inversion (b)

to inversion. It should be noted that in this determination the by-pass direction about $\overset{\circ}{e}_1$ is connected not with the direction of vector e_1 but with the directions of vectors e_2 and e_3.

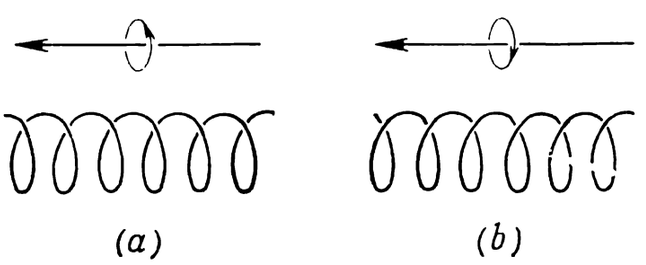


Fig. 23.7. Polar and axial vectors brought into coincidence forming right-thread (a) and left-thread (b) screws

On the contrary, the connection of the by-pass direction about vector $\overset{\circ}{e}_1$ with the direction of vector e_1 is not invariant with respect to inversion rotations. It is a polar vector together with an axial vector matched with it that form a right-handed or a left-handed screw (Fig. 23.7). Determination of the direction of rotation according to the numeration of polar vectors ensures the formation of a screw of the same thread by the other two pairs of base vectors. This means that the basis has the same handedness. Under proper rotation, screws of each thread retain their sense, while under inver-

sion rotations the thread of the screws is reversed. The sense of the basis is reversed accordingly.

But the triplet of vectors of a polar basis can also be right- or left-handed (the triplet is called right-handed if vector $\boldsymbol{e}_1$ can be matched with the thumb, $\boldsymbol{e}_2$ with the index finger, and $\boldsymbol{e}_3$ with the middle finger of the right hand). Under proper rotations both the right- and left-handed triplets retain their handednesses while under inversion rotations the right-handed triplet becomes left-handed, and the left-handed triplet becomes a right-handed one.

When the by-pass directions about axial vectors are determined according to the numeration of the polar vectors matched with them the two bases are in agreement: the thread of the screw formed by the pairs of matched vectors coincides with the handedness of the polar vectors triplet; if, for example, $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$ form a right-handed triplet, then the screws formed by vectors $\boldsymbol{e}_1$ and $\overset{\circ}{\boldsymbol{e}}_1$, $\boldsymbol{e}_2$ and $\overset{\circ}{\boldsymbol{e}}_2$, $\boldsymbol{e}_3$ and $\overset{\circ}{\boldsymbol{e}}_3$ are also right-handed. This agreement of the polar and axial bases is invariant with respect to any orthogonal transformations.

Thus to a given polar basis there corresponds one and only one axial basis, the connection between them remaining unchanged under any orthogonal transformations, on the contrary, two polar bases correspond to each axial basis. This allows referring the components of not only the polar, but also of axial vectors to a polar basis. When a polar basis is orthogonally transformed $\boldsymbol{e}_{i'} = c_{i'k}\boldsymbol{e}_k$, the axial basis related to it is transformed in accordance with relation $\overset{\circ}{\boldsymbol{e}}_{i'} = \overset{\circ}{c}_{i'k}\overset{\circ}{\boldsymbol{e}}_k$, $\overset{\circ}{c}_{i'k}$ being equal to $c_{i'k}$ in proper rotations and to $-c_{i'k}$ in the inversion rotations. Denoting $\Delta = \det \| c_{i'k} \|$ this can be written as

$$\overset{\circ}{c}_{i'k} = \Delta c_{i'k}. \tag{23.5}$$

Coefficients a_i of the expansion

$$\overset{\circ}{\boldsymbol{a}} = a_i \boldsymbol{e}_i \tag{23.6}$$

of the axial vector $\overset{\circ}{\boldsymbol{a}}$ in terms of the polar basis are equal, by definition, to the coefficients $\overset{\circ}{a}_i$ of its expansion in terms of the axial basis connected with the given polar basis; they can be simply called the components of axial vector $\overset{\circ}{\boldsymbol{a}}$. Their transformation law follows from the comparison of (23.4) and (23.5):

$$a_{i'} = \Delta c_{i'k} a_k. \tag{23.7}$$

From (23.6) it follows that the components of the axial vector

$$a_i = \overset{\circ}{\boldsymbol{a}} \cdot \boldsymbol{e}_i \tag{23.8}$$

are the scalar products of the axial and the polar vector.

In the general case, the scalar product of axial vector $\overset{\circ}{\boldsymbol{a}} = a_k \boldsymbol{e}_k$ and polar vector $\boldsymbol{p} = p_l \boldsymbol{e}_l$ is equal to

$$\overset{\circ}{\boldsymbol{a}} \cdot \boldsymbol{p} = (a_k \boldsymbol{e}_k) \cdot (p_l \boldsymbol{e}_l) = a_k p_k. \tag{23.9}$$

Its transformation law follows from the transformation laws for the components of axial (23.7) and polar (18.1) vectors:

$$a_{i'} p_{i'} = \Delta c_{i'k} a_k c_{i'l} p_l = \Delta \delta_{kl} a_k p_l = \Delta a_k p_k \tag{23.10}$$

(equation (17.4) has been used here). Thus this scalar product is invariant with respect to the proper rotations of the coordinate system

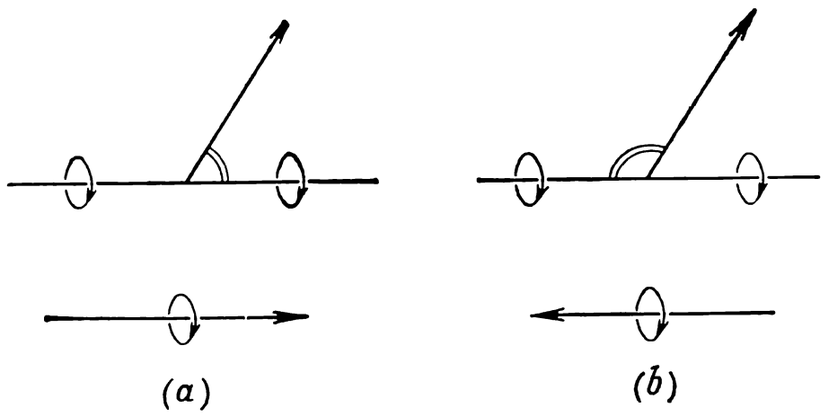


Fig. 23.8. On determination of the angle between polar and axial vectors: (a) angle between polar and axial vectors in a right-handed system of coordinates; (b) angle between the same vectors in a left-handed system of coordinates

and is multiplied by —1 under inversion rotations. These quantities are called *pseudo-scalars*; the law of their transformation appears as

$$\psi' = \Delta\psi \tag{23.11}$$

where ψ is the pseudo-scalar component in the old system of coordinates, ψ' is that in the new system, and Δ is the determinant of the orthogonal transformation matrix changing the old system into the new one.

An example of a pseudo-scalar is the quantity of specific rotation of the polarization plane of isotropic or optically isotropic substances that rotate the polarization plane (an aqueous solution of sugar, cubic crystals of $NaClO_3$ and $NaBrO_3$, ect.). This quantity is considered positive if the direction of rotation of the polarization plane is specified by a screw differing from that of the coordinate system and negative, in the opposite case (see Sec. 81). As under the inversion rotation of a coordinate system the thread of its screw changes, the quantity of specific rotation with respect to the new coordinate system and the same quantity with respect to the old one will have opposite signs. Usually the specific rotation is given with respect to a right-handed coordinate system.

The scalar product of an axial vector by a polar one can also be determined purely geometrically (Fig. 23.8): it is equal to the product of vector lengths by the cosine of the angle between them. Out of the two possible angles (complementing each other to π) such an angle is chosen that in rotation of one of the two vectors through it up to the coincidence with the second vector, the resulting screw

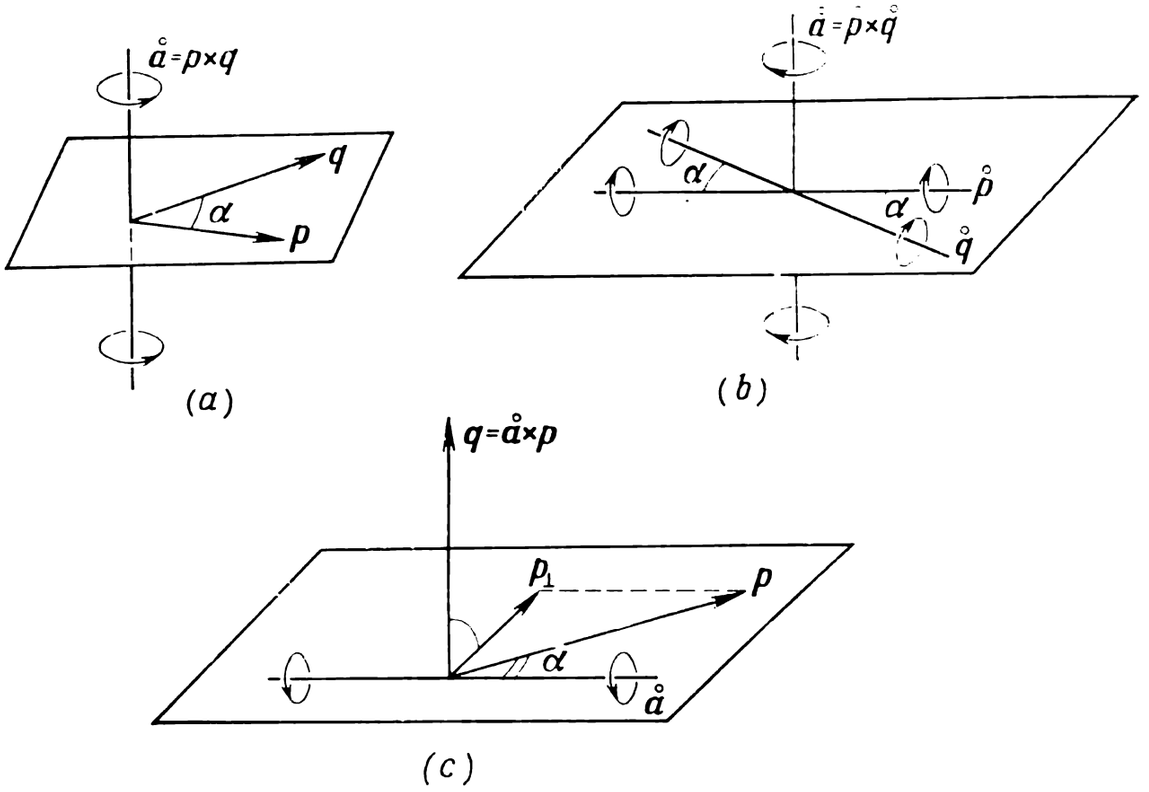


Fig. 23.9. Vector products: (a) of two polar vectors; (b) of two axial vectors; (c) of an axial and a polar vector

is of the same thread as the basis (or the coordinate system constructed on it). Thus the scalar product of polar and axial vectors has sense only when a definite coordinate system is given or more exactly, when the handedness of the system is known.

Let us now consider vector products. The vector product of two polar vectors $\boldsymbol{p} \times \boldsymbol{q}$ is, by definition, an axial vector $pq \sin\alpha$ long, perpendicular to both factors of the product, and the direction of its rotation coincides with the direction of rotation which matches the first factor of the product with the second one (Fig. 23.9*a*).

The vector product of two axial vectors is determined in the same way (Fig. 23.9*b*).

The vector product of an axial vector by a polar one $\mathring{\boldsymbol{a}} \times \boldsymbol{p}$ is a polar vector, q, $ap \sin\alpha$ long, perpendicular to both factors of the product, and directed in the same way as the component $p_\perp$ of vector $\boldsymbol{p}$ perpendicular to $\mathring{\boldsymbol{a}}$ if it were rotated through $\pi/2$ about vector $\mathring{\boldsymbol{a}}$ in the direction of its circuit (Fig. 23.9*c*). The fact of the angle between polar and axial vectors being somewhat indefinite is of no impor-

tance, since $\sin(\pi - \alpha) = \sin \alpha$. When the factors of the product are permuted, the direction of this vector product, as well as of those discussed earlier, changes for the opposite one.

The components of all these vector products can be written in a single form; let $\boldsymbol{c} = \boldsymbol{b} \times \boldsymbol{d}$, where each of the vectors $\boldsymbol{b}$ and $\boldsymbol{d}$ can be regarded either as a polar or an axial vector, while the type of vector $\boldsymbol{c}$ is determined by the types of vectors-cofactors of the product. Then

$$c_i = \delta_{ijk} b_j d_k. \tag{23.12}$$

This form can also be used for writing a differential operation curl. It is known that a vector function of coordinates $\boldsymbol{u} = \operatorname{curl} \boldsymbol{v}$ can be represented as $\boldsymbol{u} = \nabla \times \boldsymbol{v}$, where the symbolic vector $\nabla = \boldsymbol{e}_i \frac{\partial}{\partial x_i}$. Therefore the components of vector $\boldsymbol{u} = \operatorname{curl} \boldsymbol{v}$ are equal to

$$u_i = \delta_{ijk} \frac{\partial v_k}{\partial x_j}. \tag{23.13}$$

The fundamentals of tensor calculus are given in a number of manuals and handbooks, e.g. Akivis and Goldberg (1969); Borisenko and Tarapov (1966); Vakulenko (1972); Rashevsky (1964); Shouten (1965). Besides, in some monographs and textbooks on mechanics of continuous media and on crystal physics there are sections on tensor calculus: Lurie (1970); Sedov (1962, 1970); Fedorov (1965, 1975); Nye (1957); Wooster (1938, 1958, 1977). See also Sirotin (1960, 1960a, 1961, 1964).

Chapter III

INTRODUCTION TO CRYSTAL PHYSICS. ELECTRICAL AND THERMAL PROPERTIES OF CRYSTALS

Sec. 24. Anisotropic Continuous Media

The basic initial concept of any theory of a continuous medium is its *elementary volume*, i.e. a mentally isolated part of the studied material, of the dimensions satisfying two requirements: (1) the isolated part should contain so many structural units (in case of a crystal— unit cells, in case of fiber glass-reinforced plastic— individual glass fibers etc.) as it could be assumed homogeneous with sufficient accuracy; (2) it should be small enough to allow ignoring the variations of physical fields throughout its extent: within an elementary volume physical fields (electric, magnetic, stress fields, etc.) are regarded as uniform. Denoting the lattice constant by a, the typical dimension of elementary volume as $\sqrt[3]{v}$, and the field gradient as $\partial E/\partial x$ (of an electric field, for a definite example), the two requirements can be written in the following way:

$$a \ll \sqrt[3]{v} \ll \frac{E}{\partial E/\partial x}. \tag{24.1}$$

If the field is periodic in space and is characterized by wavelength λ, then (24.1) takes the form

$$a \ll \sqrt[3]{v} \ll \lambda. \tag{24.2}$$

It does not follow from the continuous medium being homogeneous within the limits of its elementary volume that it is homogeneous on the whole, i.e. that the properties of all its elementary volumes are the same. It only follows that the properties of continuous elementary volumes are closely similar. Considering dielectric permittivity $\varkappa$ as an example, the following condition can be written for any continuous medium

$$a \ll \sqrt[3]{v} \ll \frac{\varkappa}{\partial \varkappa/\partial x},$$

or $\frac{\partial \varkappa}{\partial x} \ll \frac{\varkappa}{d}$, while in a homogeneous medium

$$\frac{\partial \varkappa}{\partial x} \equiv 0.$$

Discussing the influence on a crystal of physical fields whose wavelengths greatly exceed the dimensions of the unit cell, we can digress

from the microscopic crystal structure and imagine the crystal to be some continuous medium. On the contrary, the discrete structure of a crystal becomes manifest in the effects of interaction between the crystal substance and the fields whose wavelengths are comparable to the dimensions of the unit cell; this allows using the effects for studying the crystal structure.

In this book crystals are regarded as homogeneous anisotropic continuous media*. A medium is called *homogeneous and anisotropic* when its properties do not depend on the Cartesian coordinates, although they depend on the direction. Parallel directions are considered as one direction, and parallel planes, as one plane.

Sometimes such media are called *rectilinear-anisotropic*, in distinction from *curvilinear-anisotropic* ones—for instance, cylindrically- or spherically anisotropic media. We shall regard only rectilinear anisotropic media as homogeneous. It is desirable that the definition of homogeneity be invariant, i.e. that a material would be considered as homogeneous or non-homogeneous regardless of the system of coordinates in which it is studied. For this purpose it is necessary that the covariant derivatives, and not the partial ones, with respect to the coordinates of the tensors which characterise the properties of the material be zero. Insofar as for the equivalence to zero of the covariant derivatives with respect to any curvilinear coordinates it is necessary and sufficient to have the equivalence to zero of the partial derivatives with respect to the Cartesian coordinates, only rectilinear anisotropic materials are truly homogeneous.

The anisotropy of the physical properties of crystals is determined by measuring these properties in differently oriented crystal specimens. Thus the anisotropy of thermal expansion in crystals can be determined by measuring the relative changes in thickness, $\Delta a/a$, of differently oriented crystals during their heating. The *coefficient of thermal expansion* for a plate whose orientation is specified by the Miller indices (hkl) is equal to

$$\alpha_{(hkl)} = \frac{(\Delta a/a)_{(hkl)}}{\Theta}.$$

where Θ is the difference in temperatures before and after heating. Similarly, the anisotropy of Young's modulus is found by measuring the relative elongation, $\Delta l/l$, of differently oriented crystal rods due to the action of tensile stress σ: for rod $[uvw]$ *Young's modulus* is $E_{[uvw]} = \frac{\sigma}{\Delta l/l_{[uvw]}}$. Elastic properties of materials are specified not only by the Young's modulus, but also by the torsion modulus of cylinder G. Measuring the relative angles, φ/l, of twist of differently oriented round crystal rods due to the action of torque K, we obtain for the rod $[uvw]$ the *modulus of twisting* $G_{[uvw]} = \frac{K/J}{(\varphi/l)_{[uvw]}}$

* The study of the defects of crystal structure and of their influence on the physical properties of crystals is outside the scope of this book.

where J—is the polar moment of inertia of the rod cross-section. Often use is made of reciprocal quantities E^{-1} and G^{-1}; they are called the *coefficient of tension* and the *coefficient of twisting**.

The orientation of crystal rods and plates can also be specified by a unit vector $\boldsymbol{n}$ directed along the rod axis or along a perpendicular to the plate (on the connection of the vector components with Miller indices see Sec. 16). The components n_i of vector $\boldsymbol{n}$ can in turn be expressed with the aid of formulas (22.5) in terms of spherical coordinates—angles ϑ and φ (see also Fig. 22.1). Ultimately the coefficient of thermal expansion, Young's modulus, and the modulus of cylinder twisting are represented as functions of unit vector, α ($\boldsymbol{n}$), E ($\boldsymbol{n}$), G ($\boldsymbol{n}$) or of spherical coordinates α (ϑ, φ), E (ϑ, φ), G (ϑ, φ).

If from a certain point O—the origin of a spherical system of coordinates—all possible beams are drawn, specified by angles ϑ and φ, and values α (ϑ, φ) or E (ϑ, φ) are plotted on the beams according to some scale, *representation surfaces* of the coefficient of thermal expansion and Young's modulus will be obtained, the models of such surfaces for some crystals are shown in Figs. 24.1-24.10. Making the models of representation surfaces is a complicated process, and the models, although lucid, are not very suitable for quantitative assessments. Somewhat more convenient in this respect are the *sections of representation surfaces* (see Figs. 24.5, 24.8*b*, 24.10). But even they allow a numerical assessment of the property they represent only in some directions. Sometimes a representation surface is the surface of revolution and its section permits the assessment in all directions (see Figs. 24.3 and 24.6). In other cases stereographic projections of representation surfaces are needed (Butabayev and Sirotin, 1972, 1973; Sirotin and Yanusova, 1977). In these projections physical properties are shown graphically as contour lines. As was shown in Sec. 2, to each direction in space there corresponds a definite point in stereographic projection. To each direction in a crystal there corresponds in turn a definite value of an anisotropic physical property. Connecting those points in stereographic projection which are characterized by the same magnitude of a physical property, we obtain a contour line of this property, while all the lines together constitute the stereographic projection of the representation surface of this physical property (see Figs. 24.1*b*, 24.2*b*, 24.11).

Let us consider, for instance, Fig. 24.1b—the stereographic projection of the representation surface of the coefficient of thermal expansion of aragonite, the surface itself being shown in 24.1*a*. It is known (see Sec. 2) that to each direction of the upper hemisphere

* These quantities are discussed in more detail in Ch. VI: the coefficient of thermal expansion in Sec. 51 and Sec. 52, Young's modulus in Sec. 53, the torsion modulus of a cylinder in Sec. 54.

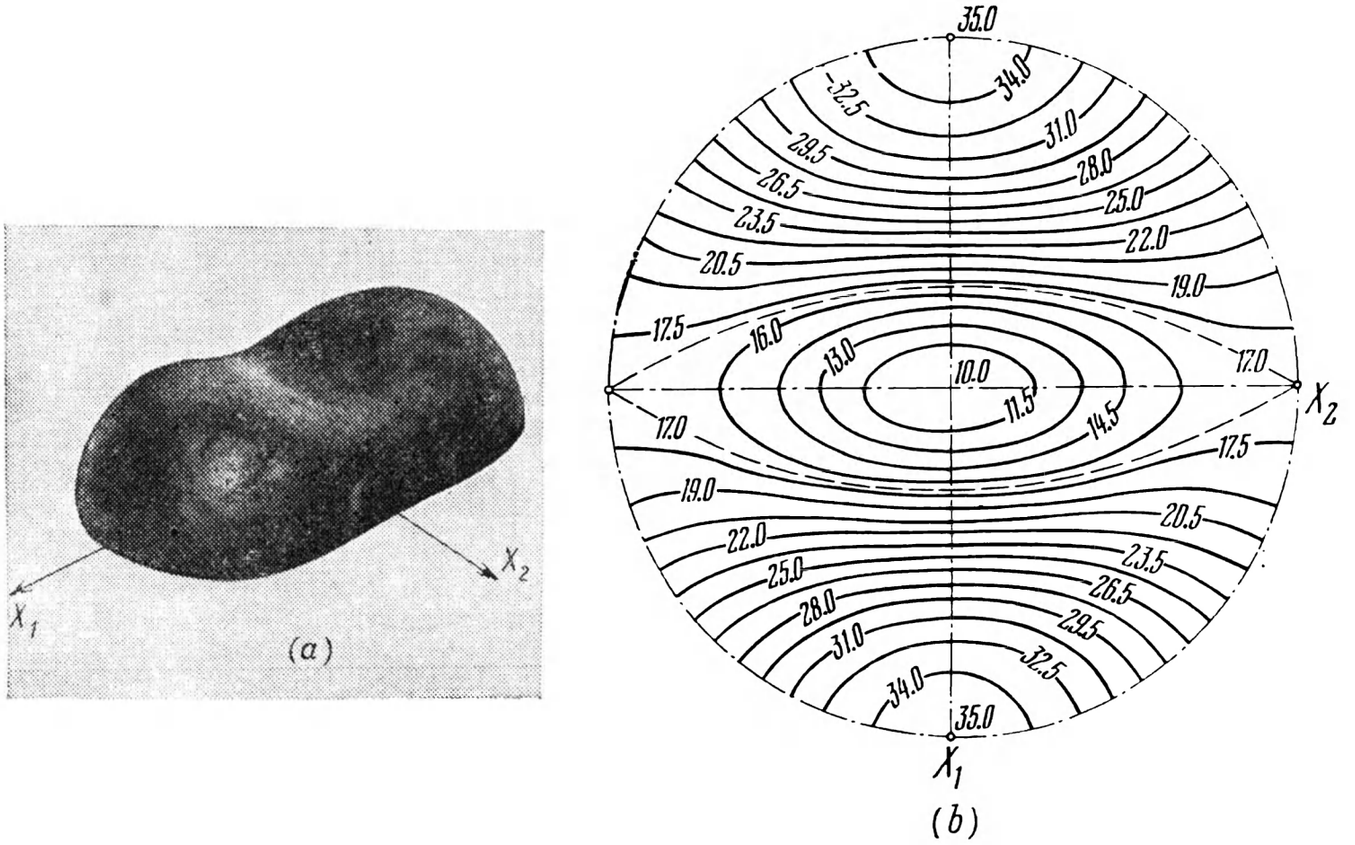


Fig. 24.1. Model of the upper half (the lower half is its mirror reflection) of the representation surface of the thermal expansion coefficient of an aragonite crystal, class *mmm* (a) and its stereographic projection (in 10^{-6} K^{-1}) (b) (Butabayev and Sirotin, 1973)

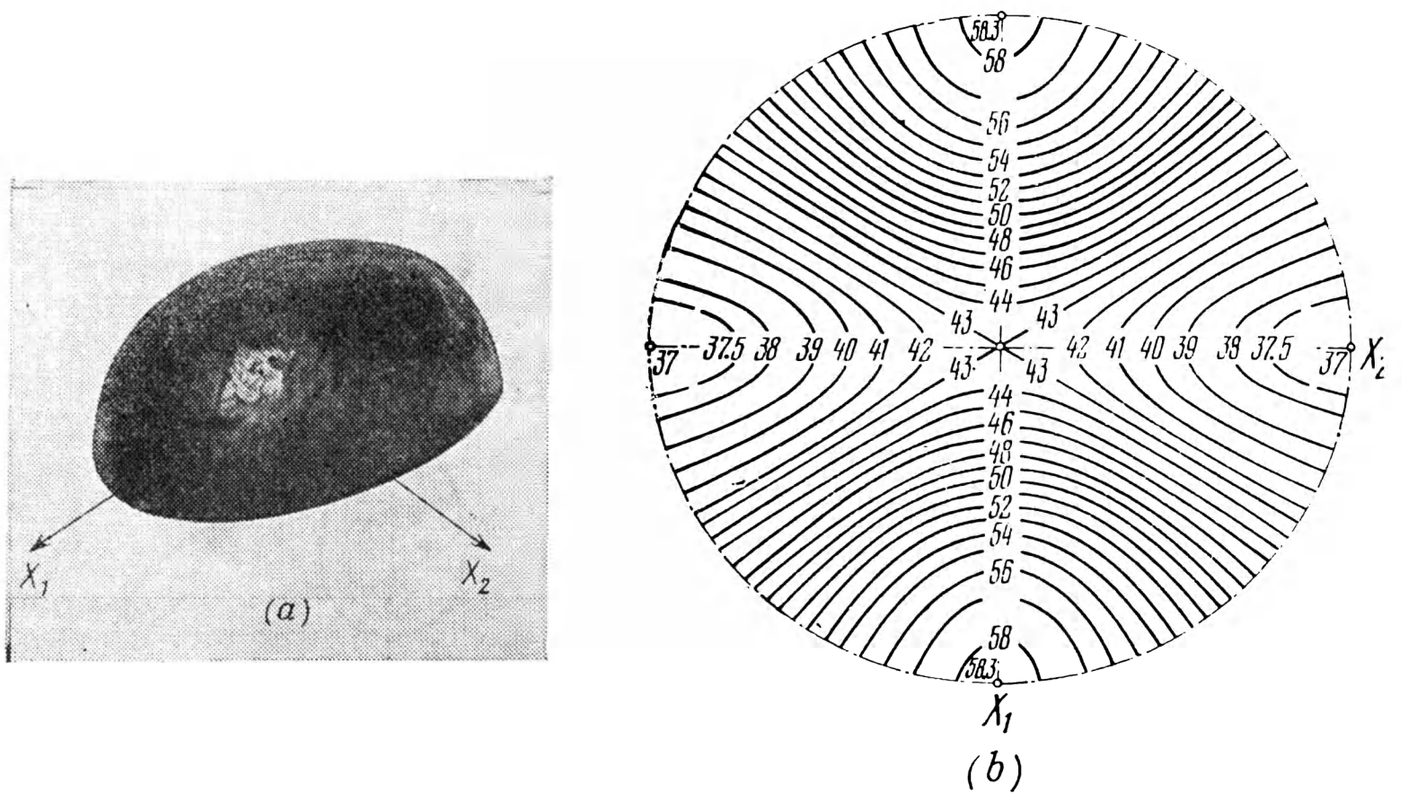


Fig. 24.2. Model of the upper half (the lower half is its mirror reflection) of the representation surface of the thermal expansion coefficient of a Rochelle salt crystal, class *222* (a) and its stereographic projection (in 10^{-6} K^{-1}) (b). The difference in stereographic projections in Figs. 24.1 and 24.2 is due to the fact that in aragonite there corresponds to the centre of projection (axis X_3) the extreme value of function α (ϑ, φ), while in the Rochelle salt, the saddle point of this function (Butabayev and Sirotin, 1973)

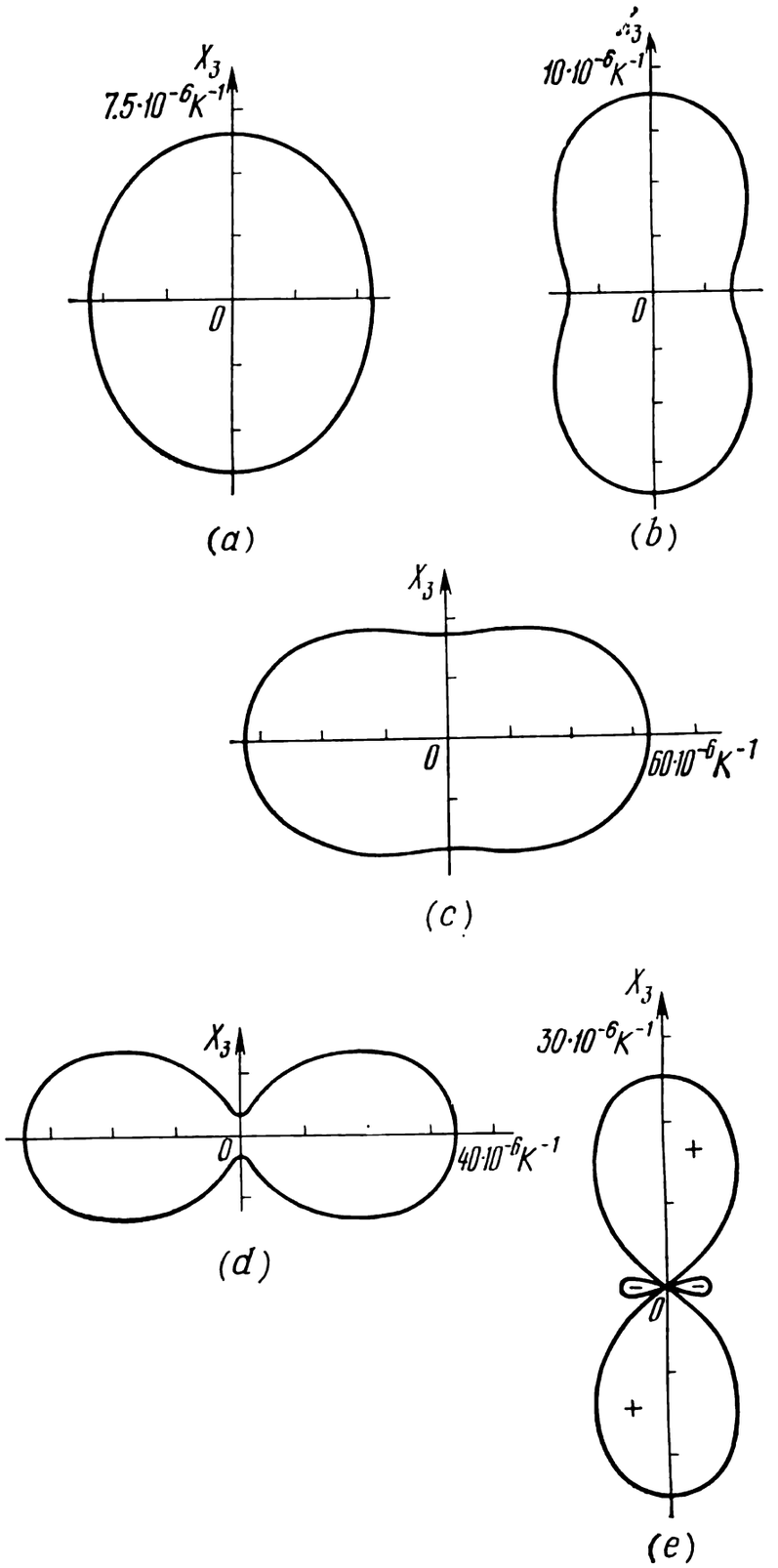


Fig. 24.3. Sections of the representation surfaces of revolution for a thermal expansion coefficient (a) for a sapphire crystal, class $\bar{3}m$; (b) for tourmaline, class $3m$; (c) for potassium dihydrophosphate (KDP), class $\bar{4}2m$; (d) for ammonium dihydrophosphate (ADP), class $\bar{4}2m$; (e) for calcite, class $\bar{3}m$ (Butabayev and Sirotin, 1972)

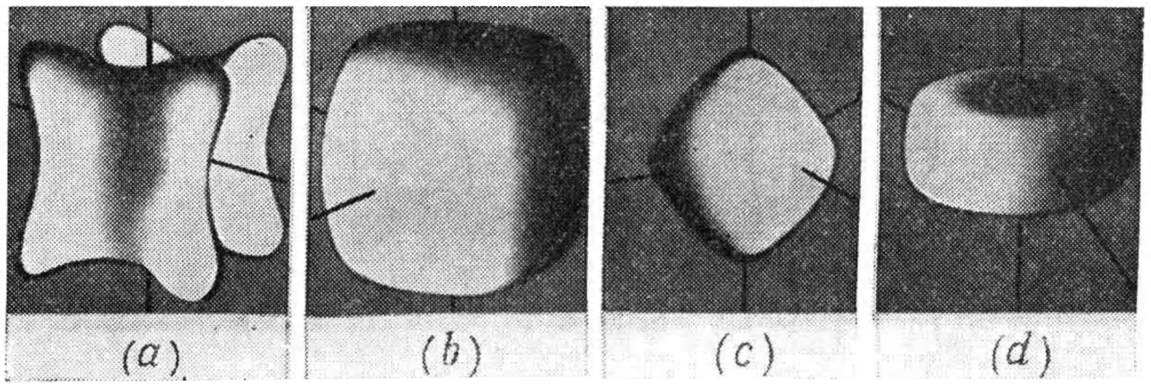


Fig. 24.4. Models of the representation surfaces of Young's modulus: (a) for a monocrystal of gold, class $m3m$; (b) for aluminium, class $m3m$; (c) for magnesium, class $6/mmm$; (d) for zinc, class $6/mmm$. The symmetry of the first two surfaces is $m3m$, of the others, ∞/mm (Kleber, 1977)

there corresponds a definite point in the circle of the stereographic projection. The lines on the stereographic projection of the representation surface connect the points that correspond to those directions in which the coefficient of thermal expansion of aragonite is the same, i.e. those where α (ϑ, φ) = 10.0; 11.5; 13.0; . . .; 32.5; 34.0; $35.0 \cdot 10^{-6}$ K^{-1}. These are the contour lines of the function α (ϑ, φ).

The stereographic projections of representation surfaces can be used as nomograms for determining the quantity specifying a particular property in any given direction, or for determining the directions in which this quantity has a given (in particular, an extreme) value. For this purpose a polar net of the same diameter as the projection is needed; it can be drawn on transparent paper. If crystallographic planes and directions are plotted on the net, it is possible to determine also the quantitative characteristics of the properties, for instance, $\alpha_{[hkl]}$, $E_{[uvw]}$ or $G_{[uvw]}$ (Butabayev and Sirotin, 1975).

Many quantities specifying the properties of crystals in all directions are positive; such are Young's modulus and the modulus of

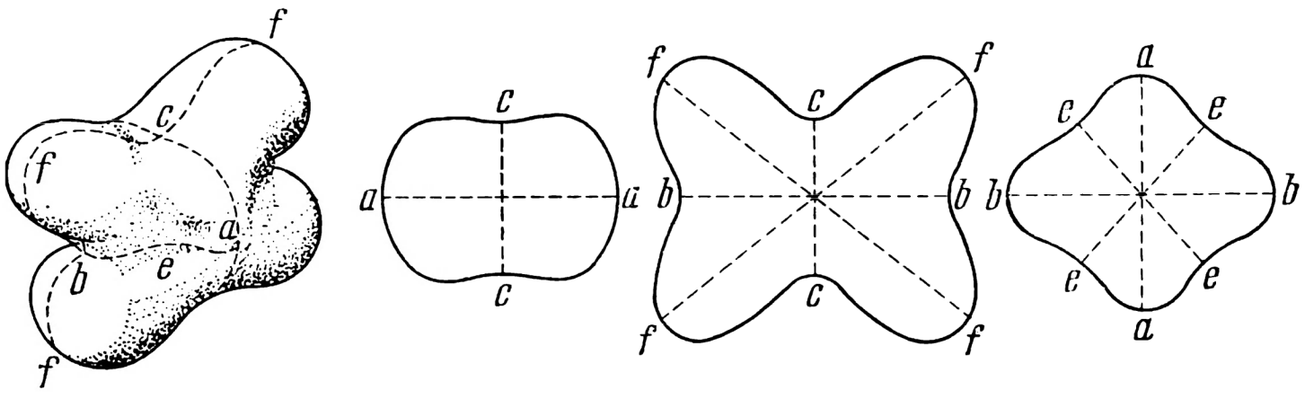


Fig. 24.5. Representation surface of the tension coefficients of a baryte crystal, class mmm, and its sections; letters a, b, . . . indicate the locations of the sections with respect to the surface (Groth, 1897)

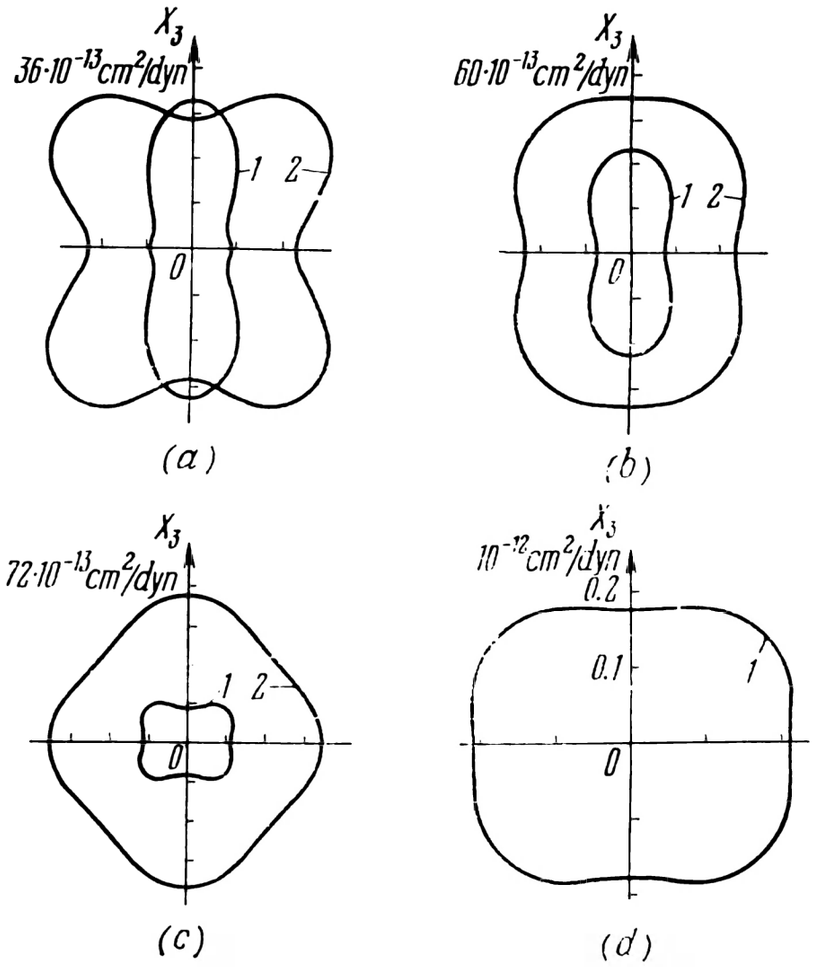


Fig. 24.6. Sections of the representation surfaces of revolution for elastic properties: (a) for zinc crystals, class $6/mmm$; (b) for cadmium, class $6/mmm$; (c) for cadmium sulphide (CdS), class $6mm$; (d) for α-silicon carbide, class $6mm$; *1*—section of the surface of the coefficient of tension, *2*—section of the surface of the twisting coefficient (Butabayev and Sirotin, 1972)

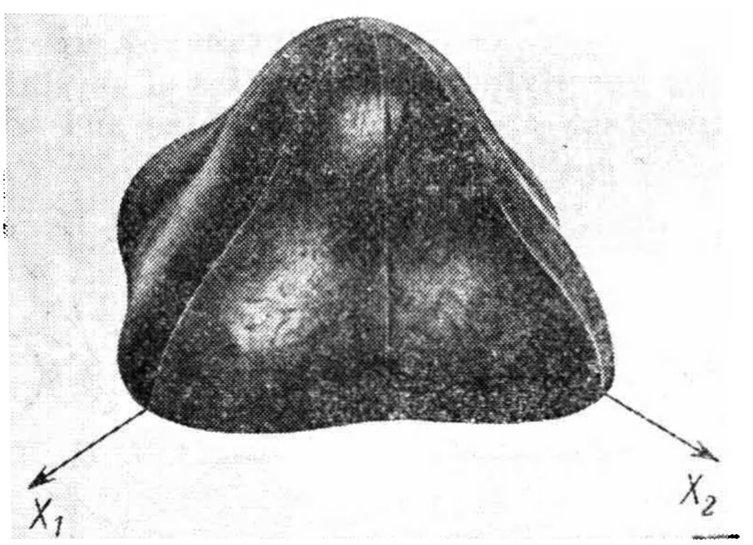


Fig. 24.7. The upper half (the lower half is its mirror reflection) of a model of the representation surface of the tension coefficient of a silicon crystal, class $m3m$ (Bytabayev and Smyslov, 1971)

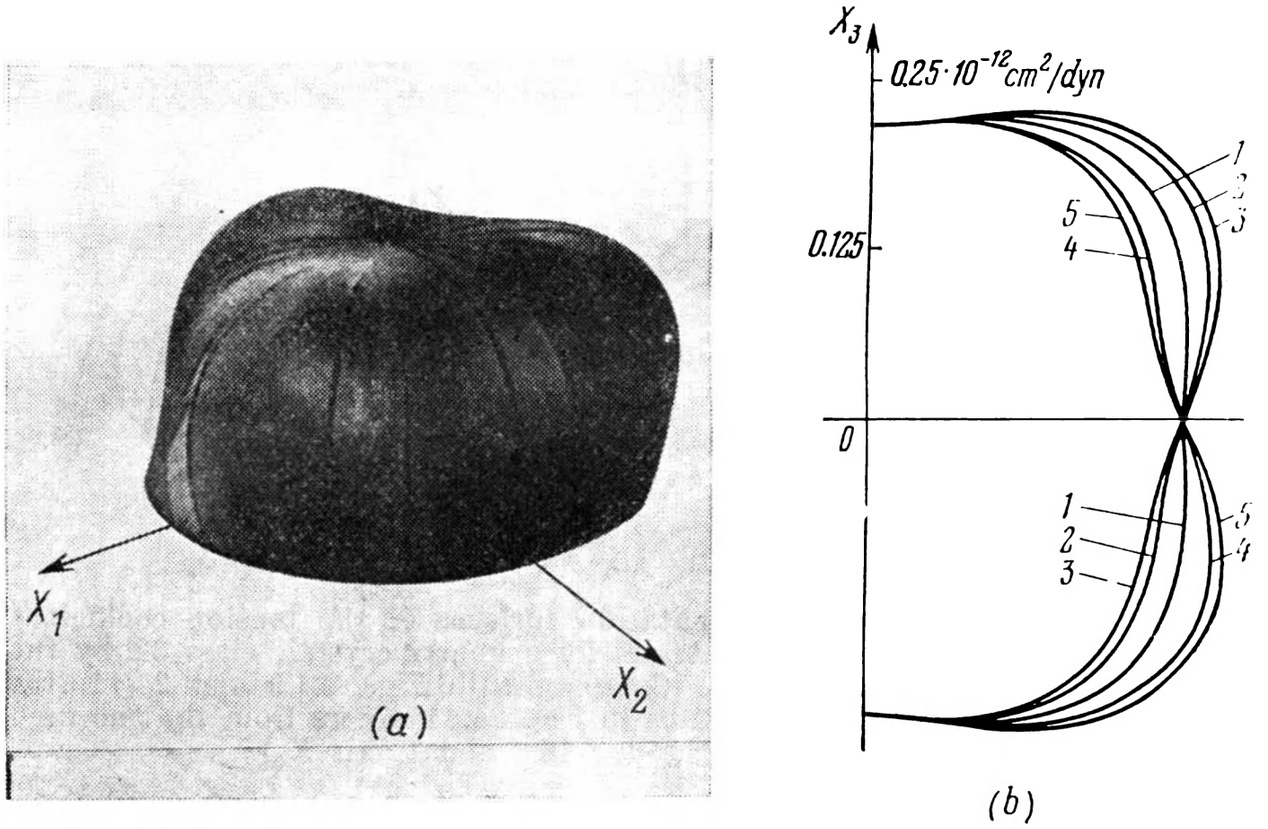


Fig. 24.8. The upper half (the lower half is obtained from the upper one by inversion in the centre) of a model of the representation surface of the tension coefficient of a sapphire crystal, class $\bar{3}m$ (a) and of sections of the representation surface by vertical planes (b): *1*—by a plane passing through X_1, *2*—by a plane +15° away from the first one, *3*—by +30°, *4*—by —15°, *5*—by—30° away from the first, the signs of the angles correspond to rotation toward the positive (+) or negative (—) end of axis X_2 (Butabayev and Smyslov, 1971)

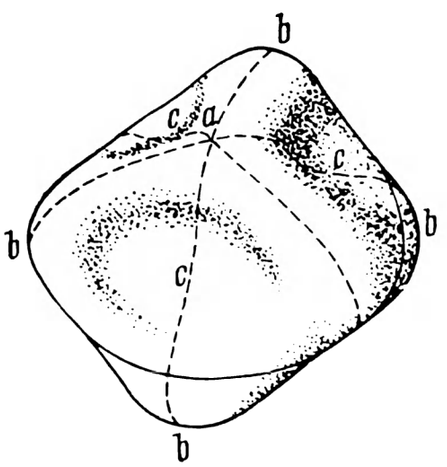


Fig. 24.9. Representation surface of the tension coefficient of a quartz crystal, class 32: *a*—emergence of direction [0001], *bb* and *cc*—the ends of the three largest and three smallest diameters. A solid line indicates the circular section of the representation surface by plane (0001). Dashed lines indicate the sections of the representation surface by planes $\{2\bar{1}\bar{1}0\}$. Symmetry of the surface is $\bar{3}m$ (Groth, 1897)

cylinder torsion, but there are some which can have both positive and negative values, e.g. the coefficient of thermal expansion of calcite (Fig. 24.3*e*). The parts of a representation surface correspond-

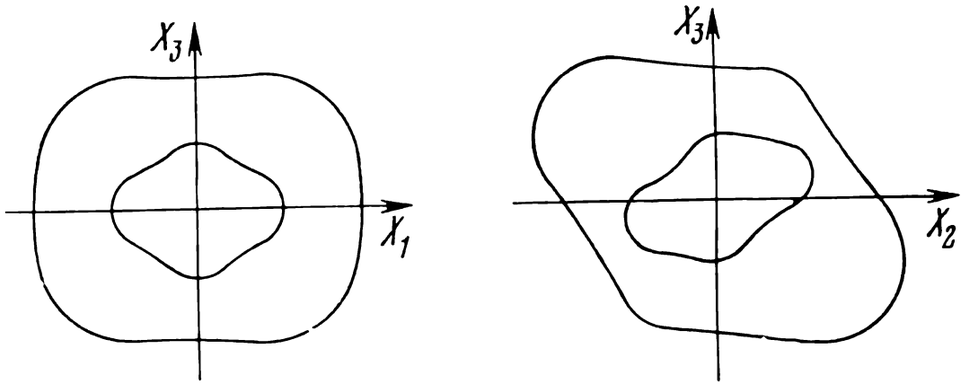


Fig. 24.10. Sections of the representation surfaces of the tension coefficient (inside) and twisting coefficient (outside) for a quartz crystal, class 32, by the coordinate planes (Wooster, 1949). Compare with Figs. 24.9 and 24.11 (the crystallographic system of coordinates in Fig. 24.11 differs from the one used here in rotation through 180° about axis X_3)

ing to such negative values are shown black in contrast to its positive, white parts (compare the representation surfaces of vectors and second-rank tensors, Figs. 22.3, 22.2), or are simply marked with the "minus" or "plus" signs.

Sec. 25. The Symmetry Principle in Crystal Physics

From the standpoint of crystal physics, the 39 crystallographic and limit classes are 39 possible types of interaction between the anisotropy and the symmetry of a continuous medium, 39 types of opposition, or antagonism, between these two factors. One of them—class 1—is characterized by the unconditional victory of anisotropy: in crystals of this class anisotropy is fully manifest, without any constraints. Two limit classes—$\infty\infty\infty m$ and $\infty\infty$ — are noted for its just as decisive defeat: in media with such a symmetry all the directions are equivalent, this meaning that no anisotropy is possible in them. Each of the other 36 classes is characterized by strictly definite limitations on the anisotropy of different physical properties. These limitations are a logical consequence of the symmetry of crystals.

The subject of the influence of the crystal symmetry on crystal properties is only a part of the more general subject on the role of symmetry in physics and, moreover, in theoretical natural science on the whole*. The general principle, defining the influence of symmetry

* See Shubnikov (1956a); Shubnikov and Koptsik (1972).

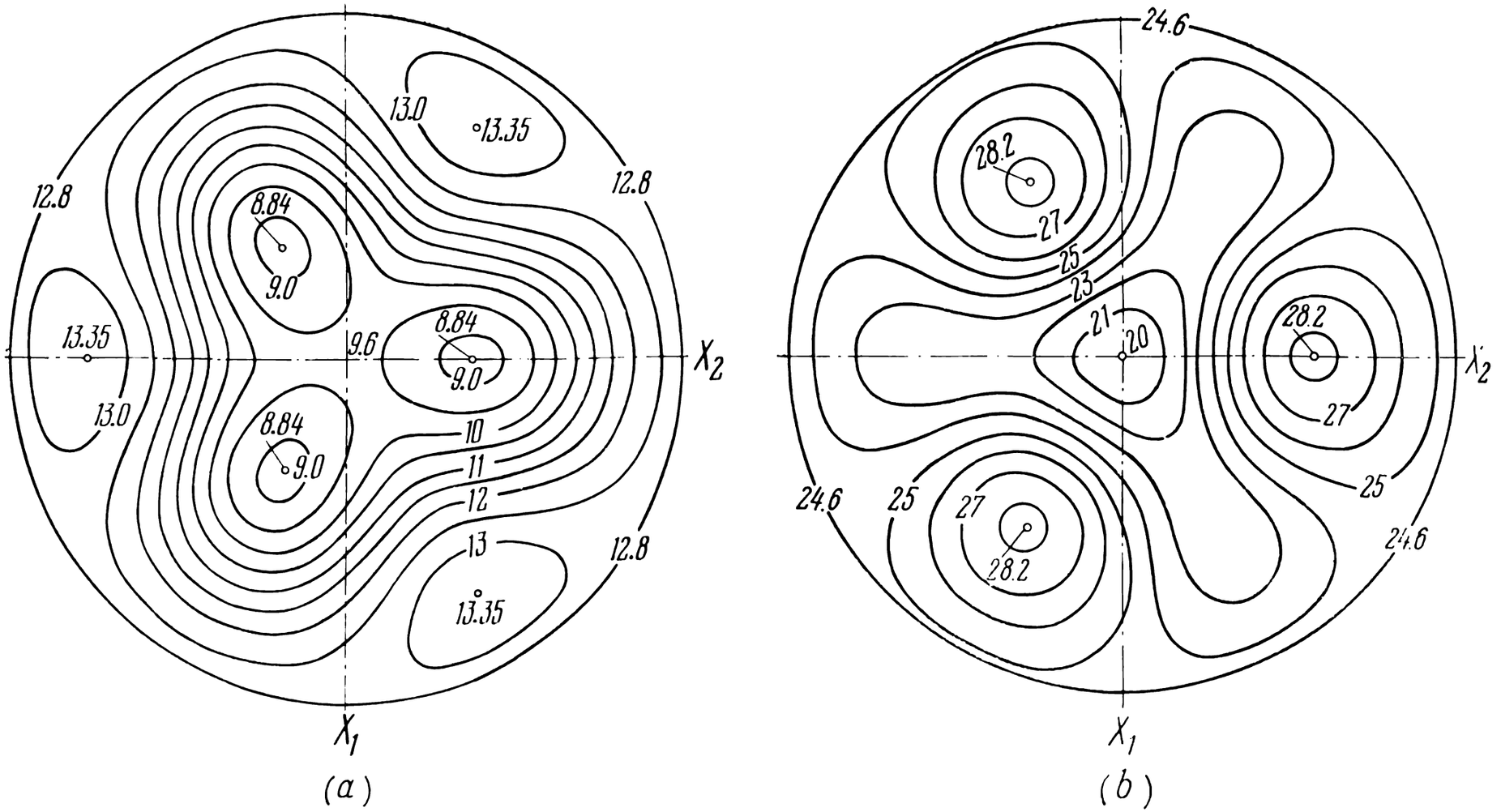


Fig. 24.11. Stereographic projections of the representation surfaces of the tension (a) and twisting (b) coefficients of a quartz crystal, class 32; in 10^{-13} cm/dyn. The lower circles of the stereographic projections are obtained from the ones rotated through 180° about axis X_1. It can be seen that planes $\{2\bar{1}\bar{1}0\}$ (in particular, plane X_2, X_3) are the symmetry planes of these surfaces, the point group of which is thus equal to $\bar{3}m$. Compare with Figs 24.9 and 24.10

on all the physical phenomena, without exception, was formulated by Pierre Curie in 1893-1895: "When definite causes produce definite effects, the elements of symmetry of the causes should be apparent in the effects.

When definite dissymmetry is found in some phenomena, the same dissymmetry should be found in the causes that produced them*.

Any reverse postulates are wrong, at least in practice; in other words, effects can have higher symmetry than their causes"**.

All the properties of crystals depend on their structure. Therefore Curie's principle with respect to the properties of crystals states that all the symmetry elements of a crystal are at the same time the symmetry elements of any of its properties; and conversely, any dissymmetry of any crystal property testifies to a corresponding dissymmetry in a crystal structure.

This statement can be defined more accurately. Considering any macroscopic property of a crystal, it is necessary to regard cell parameters as being physically infinitesimal, this meaning that the elementary translations included in the space group of the crystal are also infinitesimal. Hence two important conclusions follow. First, the translation symmetry of a crystal means the homogeneity of the crystal with respect to any macroscopic property; in other words, if the crystal is regarded as a continuous medium, it should be regarded as a homogeneous continuous medium. Second, if elementary translations are infinitesimal, their fractions are all the more minute; consequently, the differences in rotation and screw axes, in mirror and glide planes are quite inessential for the macroscopic properties. Thus the symmetry of the macroscopic properties of crystals is determined by the point group of crystal symmetry, and not by the space one; this conclusion coincides with the well-known Neumann's principle (1885), the latest wording of which is this: "The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal"***. So, Neumann's principle can be regarded as the consequence of Curie's principle, although it preceded the latter and played an important role in the development of crystal physics. In Nye's well-known textbook (1957) Neumann's principle is called "a fundamental postulate of crystal physics"; here we derive it from Curie's prin-

---

* There is a distinction between "asymmetry" and "dissymmetry". "In accordance with the morphology of these words—writes A. V. Shubnikov (1951, p. 160)—asymmetry should be understood as the absence of symmetry, while dissymmetry as the disturbance of symmetry."

** The citation of P. Curie is from M. Curie (1909, p. 22).

*** The fundamental importance of this statement for theoretical crystal physics was many times emphasized by Voigt (1928) who gave it the name of Neumann's principle.

ciple, and so it becomes a theorem rather than a postulate. We prefer a more general statement—Curie's principle—to Neumann's principle for a postulate. However, it cannot be called a postulate of crystal physics, since it applies to a much more extensive field.

In terms of the group theory, Neumann's principle means that the symmetry group of any crystal property includes the symmetry group of the crystal itself, i.e. the symmetry group of the crystal either coincides with the symmetry group of the property or is a subgroup of the latter:

$$G_{\text{property}} \supseteq G_{\text{crystal}}. \tag{25.1}$$

The symmetry group of any crystal property should satisfy relation (25.1). A discussion of a sufficiently extensive set of different properties of some crystal will show that the only symmetry elements common for all the properties of the set will be, without exception, the symmetry elements of the crystal point group. Thus the point group of a crystal turns out to be an intersection (a common part) of the symmetry groups of all the possible properties of the crystal (Minnigerode, 1887). Koptsik (1960) reviewed the minimum sets of properties the symmetry of which unambiguously defined the point group of crystal symmetry.

Symmetry of Representation Surfaces. It follows from Neumann's principle that all the symmetry elements of a point group of a crystal serve at the same time as the symmetry elements of the representation surface of any property of this crystal. The representation surface of a property can, however, have such symmetry elements which are absent in the crystal; for example, the symmetry of the representation surfaces of properties is often specified by Curie's limit groups. For instance, the representation surfaces of the dielectric permittivity of all the cubic crystals are spheres $\varkappa = \text{const}$; their symmetry is $\infty\infty m$. The symmetry of the representation surface of Young's modulus $E = E(\vartheta, \varphi)$ for all cubic crystals is $m3m$, even though the symmetry of a crystal itself may be less: 432, $\bar{4}3m$, $m3$ or even 23. The representation surfaces of the thermal expansion coefficient of the trigonal and tetragonal crystals (see Fig. 24.3)—crystal symmetry groups $3m$, $\bar{3}m$, $\bar{4}2m$—turn out to be subgroups of the symmetry group of surfaces ∞/mm. Such is also the symmetry of the representation surfaces of the tension and twisting coefficients shown in Fig. 24.6, while the symmetry of the crystals is $6/mmm$ and $6mm$. The symmetry of the representation surface of the tension coefficient of sapphire (see Fig. 24.8), $\bar{3}m$, coincides with the symmetry of the crystal; such is also the symmetry of the representation surfaces of the tension and twisting coefficients of quartz (Figs. 24.9-24.11), although the symmetry group of the crystal is only 32. The symmetry mmm of the representation surface of the thermal expansion coefficient of aragonite, class mmm (see Fig. 24.1) and of Rochel-

le salt, class 222 (see Fig. 24.2), coincides with the symmetry of the former crystal and exceeds the symmetry of the latter. We should emphasize that the coincidence of the symmetry of solids does not at all mean the similarity of their shapes: the representation surfaces of Young's modulus of gold and aluminium (Figs. 24.4*a*, *b*), of magnesium and zinc (Figs. 24.4*c*, *d*), of the thermal expansion coefficient of tourmaline and ammonium dihydrophosphate (ADP) (Fig. 24.3*b*, *d*) have the same symmetry but greatly differ in shape; in contrast, the representation surface of the tension coefficient of sapphire (Fig. 24.8) is fairly close in shape to the representation surface of the twisting coefficient of zinc (Fig. 24.6*a*), although their symmetry groups are different: $\bar{3}m$ and ∞/mm.

Symmetry of X-ray Photographs. Although the reason for the emergence of an X-ray photograph of a crystal is the diffraction of X-rays over its spatially periodic electron density, the symmetry of an X-ray photograph, in accordance with Neumann's principle, is determined not by the space group, but by the point group of the crystal. Moreover, the symmetry of a diffraction pattern does not depend on the presence or absence of a centre of symmetry in a crystal. Therefore, the symmetry of an X-ray photograph is determined even not by a point, but a diffraction group, or Laue class which is the senior centrosymmetric class of the subsystem which the given crystal belongs to (see Sec. 6). With the aid of Curie's principle we arrive at the conclusion that the symmetry group of an X-ray photograph G_x cannot be lower than the intersection of the diffraction group of crystal G_L with the point of the photographic plate (or photographic film) $G_{pl} = \infty m$ (the axis is perpendicular to the plane of the photographic plate)*:

$$G_x \supseteq G_L \cap \infty\, m; \tag{25.2}$$

when looking for the intersection of these groups, it is necessary to take account of the mutual arrangement of their symmetry elements. Here the Laue class is

$$G_L = \begin{cases} G, & \text{if the crystal is centrosymmetric,} \\ G + \bar{1}G, & \text{if it is not centrosymmetric.} \end{cases} \tag{25.3}$$

Thus by the symmetry of an X-ray photograph is defined the Laue class of a crystal alone, while the crystal space group is derived not from the symmetry of the X-ray photograph but from the absence of reflections from some crystallographic planes—from characteristic "extinctions".

The role of Categories in Crystal Physics. The simplest and approximate classification of crystals is their division into three catego-

* The symmetry of an X-ray beam incident on a crystal perpendicularly to the photographic plate is also specified by group G_{pl}.

ries: the higher, the intermediate, and the lower one (see Sec. 4). The point groups of all classes of the lower category are the subgroups of the *mmm* group, those of the intermediate category are the subgroups of the ∞/mm group, those of the higher category—of the $\infty\infty m$ group. But *mmm*, ∞/mm and $\infty\infty m$ are possible symmetry groups of a symmetric second-rank tensor (see Sec. 22). If crystals are divided into categories according to the symmetry of a certain property, it can be expected that this property is specified by a symmetric second-rank tensor. There are very many such properties: the character of double refraction, the peculiar features of thermal expansion, dielectric permittivity and magnetic permeability, electric conductivity and thermal conductivity of crystals are specified by the category of a given crystal. All these properties are actually specified by symmetric second-rank tensors (see, e.g., Sec. 27).

The character of the anisotropy of the properties that are specified by a symmetric second-rank tensor is defined by the subdivision of crystals into categories: crystals of the higher category are isotropic with respect to these properties (group $\infty\ \infty\ m$), crystals of the intermediate category are similar to textures as to the anisotropy of these properties (group ∞/mm), and only in the lower category crystals the anisotropy of these properties is characterized by the truly crystallographic group *mmm*.

If the symmetry of a property does not fit into any of the three groups listed above, it can be said that this property, is at best described by a tensor of a higher rank. The fact that some representation surfaces of the elastic properties of crystals have an $m3m$ symmetry (Figs. 24.4*a*, *b*, and 24.7), and others a $\bar{3}m$ symmetry (Figs. 24.8, 24.9, 24.11) shows that the elastic properties of crystals cannot be described by a symmetric second-rank tensor; indeed they are described by a tensor of the fourth rank (see Secs. 51, 52).

Dissymmetry Required for Double Refraction. The second sentence of the Curie principle states that any dissymmetry found in phenomena must be contained in the causes giving rise to them. Dissymmetric phenomena can occur only in a sufficiently dissymmetric medium; a corresponding dissymmetry is either inherent in the given medium or is the result of dissymmetry of the external influence on the medium.

Let us discuss, for instance, the double refraction of light in crystals. For this phenomenon to exist the plane of the wave front in a crystal should be sufficiently dissymmetrical: it must have at least two mutually perpendicular singular directions which could serve as the directions of vibrations of the light waves propagating in the given direction. For this purpose the symmetry group of the wave front plane in the crystal should not be higher than *mmm*. On the other hand, this symmetry group is an intersection of the symmetry group of the crystal, G, with the symmetry group of the plane, ∞/mm

(the ∞ axis is perpendicular to the plane). So the condition for the existence of double refraction appears as

$$G \cap \infty/mm \subseteq mmm, \tag{25.4}$$

where the axis ∞ coincides with the direction of light propagation.

Condition (25.4) characterizes the dissymmetry of the wave-front plane in a crystal required for birefringence: none of the symmetry elements of this plane must belong to any but the *mmm* group. The symmetry elements of this group, however, are indifferent to birefringence: the latter can occur independently of the presence or absence of these elements. Thus it is the dissymmetry that the *mmm* group determines. It follows from (25.4), in particular, that no birefringence is observed when light propagates along a 3-fold symmetry axis or of a higher order; in fact, this axis is included in the intersection $G \cap \infty/mm$ which will therefore not belong to the group *mmm*. Condition (25.4) is necessary, but not at all sufficient: thus in the cubic crystals no birefringence is observed even when the direction of light propagation satisfies this condition.

If the medium itself in which light propagates has no dissymmetry required for birefringence, it can be made dissymmetrical by applying a sufficiently dissymmetrical action. Thus, for example, transparent isotropic bodies and crystals of the cubic system become birefringent under the action of uniaxial mechanical tension (piezooptical effect) or of an electric field (electrooptical effect)—see Secs. 77, 78. The principal conclusion from the above examples is in the following words of Pierre Curie: "Some symmetry elements can coexist with definite phenomena, but they are not imperatively necessary. The imperative need is for the absence of some symmetry elements. This is just the dissymmetry that creates the phenomenon".*

Sec. 26. Fundamental Equations of Electrostatics of Crystals

An electric field in a crystal, as in any dielectric, is characterized by the vector of an *electric field strength or intensity* $\boldsymbol{E}$ and the *polarization vector* $\boldsymbol{P}$. A linear combination of these vectors—an *electric induction vector* $\boldsymbol{D} = \boldsymbol{E} + 4\pi\boldsymbol{P}$ is also used. The fundamental equations of electrostatics are

$$\operatorname{curl} \boldsymbol{E} = 0, \tag{26.1}$$

$$\operatorname{div} \boldsymbol{D} = 4\pi\rho, \tag{26.2}$$

where ρ is the density of free charges. The equations are equally applicable to isotropic and anisotropic dielectrics. It follows from (26.1)

* P. Curie (1909).

that there exists a *potential* φ of the electrostatic field

$$\boldsymbol{E} = -\text{grad}\ \varphi. \tag{26.3}$$

Inside the crystal, where there are no free charges,

$$\text{div}\ \boldsymbol{D} = 0. \tag{26.4}$$

On the surface of the crystal, as at the interface of isotropic dielectrics, the tangential component $(\boldsymbol{I} - \boldsymbol{nn})\cdot\boldsymbol{E}$ of the field $\boldsymbol{E}(\boldsymbol{r})$ is continuous, while the normal component $\boldsymbol{n}\cdot\boldsymbol{D}$ of the field $\boldsymbol{D}(\boldsymbol{r})$ has a discontinuity $4\pi\rho_{\text{surf}}$ where ρ_{surf} is the surface density of free charges and $\boldsymbol{n}$ is the unit vector of a normal to the crystal surface. To the continuity of tangential components $\boldsymbol{E}(\boldsymbol{r})$ in the vicinity of the interface there corresponds the continuity of potential $\varphi(\boldsymbol{r})$ in the same neighbourhood. In a dielectric crystal near the boundary with a conductor

$$(\boldsymbol{I} - \boldsymbol{nn})\cdot\boldsymbol{E} = 0, \quad \boldsymbol{n}\cdot\boldsymbol{D} = -4\pi\rho_{\text{surf}} \tag{26.5}$$

since the field in the conductor is zero. At the boundary between two dielectrics the normal component of induction is continuous.

All the relations specified above are equally applicable to homogeneous and heterogeneous, isotropic and anisotropic dielectrics. The peculiar properties of a given dielectric: its homogeneity or heterogeneity, isotropy or anisotropy, its quantitative dielectric characteristics—all are revealed solely in the dependence of induction $\boldsymbol{D}$ or polarization $\boldsymbol{P}$ on the electric field intensity $\boldsymbol{E}$.

Let us consider, to be more definite, the dependence of $\boldsymbol{P}$ on $\boldsymbol{E}$. In isotropic dielectrics these vectors are proportional to each other:

$$\boldsymbol{P} = \alpha\boldsymbol{E} \tag{26.6}$$

where α is the *dielectric susceptibility* of the medium. To generalize (26.6) for anisotropic media, it is important to understand that this simple formula contains two statements that are entirely different in their logical nature.

1. The isotropy of a body means that until the body is placed in an electric field it has identical properties in all directions. In the latter case there appears in each elementary volume a single distinctive direction—the direction of the vector of field intensity $\boldsymbol{E}$. It follows that even if an isotropic body becomes polarized in an electric field, the vector of polarization $\boldsymbol{P}$ in each unit volume is parallel to vector $\boldsymbol{E}$ in the same volume:

$$\boldsymbol{P} \parallel \boldsymbol{E}. \tag{26.7}$$

It follows next from the isotropy that the length of vector $\boldsymbol{P}$ depends only on the length of vector $\boldsymbol{E}$ but not on its direction. Thus

$$\boldsymbol{P} = f(E). \tag{26.8}$$

Formulas (26.7) and (26.8) are logical consequences of the isotropy of the medium.

2. For deriving formula (26.6) from (26.7) and (26.8) it is necessary to make an additional statement to the effect that a functional dependence, in no way expressed concretely in (26.8), comes to direct proportionality

$$P = \alpha E. \tag{26.9}$$

This equality does not follow from any physical law and only means that in the expansion of the function $P = f(E)$ in terms of the power of E

$$P = P_0 + \left(\frac{\partial P}{\partial E}\right)_{E=0} E + \frac{1}{2}\left(\frac{\partial^2 P}{\partial E^2}\right)_{E=0} E^2 + \ldots \tag{26.10}$$

sufficient accuracy is already given by the term which contains E in the first power (in the absence of a field all directions in an isotropic body have equal rights, and since the presence of polarization would mean the existence of a distinctive direction, $P_0 = 0$)*. Comparing (26.9) and (26.10) we find

$$\alpha = \left(\frac{\partial P}{\partial E}\right)_{E=0}. \tag{26.11}$$

It is evident that in the generalization of the relations between vectors $\boldsymbol{P}$ and $\boldsymbol{E}$ for isotropic media, the assumption of the linear nature of this relation can be used, the allowance for the isotropy of the media should be replaced by the allowance for the effect of crystal symmetry on its dielectric properties.

The expansion (26.10) for anisotropic media should be evidently replaced by general expansion

$$\boldsymbol{P} = \boldsymbol{P}^{(0)} + \left(\frac{\partial P}{\partial E}\right)_{E=0} \boldsymbol{E} + \ldots, \quad P_i = P_i^{(0)} + \left(\frac{\partial P_i}{\partial E_k}\right)_{E=0} E_k + \ldots. \tag{26.12}$$

Considerations with the aid of which it was found that in expansion (26.10) the term not depending on $\boldsymbol{E}$ is zero, are not applicable to the anisotropic media. Therefore the general form of the linear dependence of polarization $\boldsymbol{P}$ on the intensity of the electric field $\boldsymbol{E}$ for the anisotropic media is as follows:

$$P = P^{(0)} + \boldsymbol{\alpha} \cdot E, \quad P_i = P_i^{(0)} + \alpha_{ik} E_k, \tag{26.13}$$

where the second-rank tensor

$$\boldsymbol{\alpha} = \left(\frac{\partial \boldsymbol{P}}{\partial \boldsymbol{E}}\right)_{E=0}, \quad \alpha_{ik} = \left(\frac{\partial P_i}{\partial E_k}\right)_{E=0} \tag{26.14}$$

* For ferroelectrics (Sec. 65) this assumption is not valid even for commonly used fields; for very strong electric fields it does not hold at all (such as the field of an electromagnetic wave of laser radiation). But in most cases this linear approximation is quite sufficient, and for the time being we shall consider only such cases.

is called the *dielectric susceptibility tensor*, and vector $\boldsymbol{P}^{(0)}$ is called the *vector of spontaneous polarization*. Hence the dependence of the electric induction $\boldsymbol{D} = \boldsymbol{E} + 4\pi\boldsymbol{P}$ on the intensity of electric field $\boldsymbol{E}$ is readily obtained:

$$\boldsymbol{D} = \boldsymbol{D}^{(0)} + \boldsymbol{\varkappa}\cdot\boldsymbol{E}, \quad D_i = D_i^{(0)} + \varkappa_{ik}E_k. \tag{26.15}$$

Here the second-rank tensor

$$\boldsymbol{\varkappa} = \mathbf{I} + 4\pi\boldsymbol{\alpha}, \quad \varkappa_{ik} = \delta_{ik} + 4\pi\alpha_{ik} \tag{26.16}$$

is called the *tensor of dielectric permittivity*, and vector $\boldsymbol{D}^{(0)} = 4\pi\boldsymbol{P}^{(0)}$ is called the *vector of spontaneous electric induction*. The induction vector can also be expressed in terms of the potential φ:

$$\boldsymbol{D} = \boldsymbol{D}^{(0)} - \boldsymbol{\varkappa}\cdot\operatorname{grad}\varphi, \quad D_i = D_i^{(0)} - \varkappa_{ik}\frac{\partial\varphi}{\partial x_k}. \tag{26.17}$$

In Sec. 57 it is proved that tensor $\boldsymbol{\varkappa}$ is symmetric:

$$\varkappa_{ik} = \varkappa_{ki}; \tag{26.18}$$

hence tensor $\boldsymbol{\alpha} = (1/4\pi)(\boldsymbol{\varkappa} - \mathbf{I})$ is also symmetric.

Let us emphasize an important distinction between the tensors* considered above: vectors of the electric field intensity $\boldsymbol{E}$, of induction $\boldsymbol{D}$, of polarization $\boldsymbol{P}$ characterize the electric field of a crystal; they all change with the change of the field. On the contrary, vectors of spontaneous polarization $\boldsymbol{P}^{(0)}$ and spontaneous induction $\boldsymbol{D}^{(0)}$, as well as tensors of dielectric susceptibility $\boldsymbol{\alpha}$ and dielectric permittivity $\boldsymbol{\varkappa}$ do not change with the change of the electric field in the crystal: they characterize the dielectric properties of the crystal itself, independently of the magnitude and the very existence of an externally applied electric field. Tensors of the first type are called *field* tensors, since they characterize the field; tensors of the second type are called *matter* ones, since they characterize crystal properties. In the physics of the isotropic and anisotropic media field tensors are determined similarly; the entire distinction between the physics of the isotropic and that of the anisotropic media is concentrated exactly in the matter tensors.

Sec. 27. Symmetry of the Dielectric Properties of Crystals

As was mentioned in Sec. 26, crystals of some classes can have electric polarization even in the absence of an external electric field, this polarization is called *spontaneous*, i.e. one developing from internal causes, without any external influence. The crystals possessing this property are called *pyroelectrics* (the sense of this term is ex-

* Tensors here also mean vectors, i.e. tensors of the first rank.

plained in Sec. 31). Let us find out to what crystallographic classes can the pyroelectric crystals belong. Spontaneous polarization is specified by a vector, this meaning that its symmetry coincides with that of a vector and is characterized by the limit group ∞m. Point groups of symmetry of pyroelectric crystals should be, according to Neumann's principle, the subgroups of this group, so that out of all the symmetry elements they alone are allowed to have only one symmetry axis of any order and the symmetry planes passing through the axis. Out of the 32 crystallographic and 7 limit point groups this requirement is met by 10 crystallographic groups and 2 limit ones:

$$1,\ 2,\ 3,\ 4,\ 5,\ 6,\ m,\ mm2,\ 3m,\ 4mm,\ 6mm,\ \infty,\ \infty m.$$

Crystals and textures of other classes, as well as gyrotropic and isotropic media cannot possess non-zero vectors of spontaneous polarization, i.e. they cannot be pyroelectrics.

If a pyroelectric crystal has an axis or a plane of symmetry, its vector of spontaneous polarization should obviously be directed along this axis or lie in this plane. Therefore, in crystals of class m, in accordance with the conventions for the choice of the crystal-physical system of coordinates, the vector of spontaneous polarization is $\boldsymbol{P}^{(0)} = P_1^{(0)}\,\boldsymbol{e}_1 + P_3^{(0)}\,\boldsymbol{e}_3$, in crystals of class 2 — $\boldsymbol{P}^{(0)} = P^{(0)}\boldsymbol{e}_2$, in crystals of classes 3, 4, 6, $mm2$, $3m$, $4mm$, $6mm$ and in textures it is $\boldsymbol{P}^{(0)} = P^{(0)}\boldsymbol{e}_3$ (here $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$ are the mutually orthogonal unit vectors of the corresponding crystal-physical axes). Only in crystals of class 1 vector $\boldsymbol{P}^{(0)}$ has a general form in the crystal-physical system of coordinates.

The vector of spontaneous polarization changes, generally speaking, with the change of external conditions. However, these changes are essentially restricted by the symmetry of the crystal. In crystals possessing a symmetry axis it can apparently change only in magnitude, while its direction, always coinciding with the symmetry axis, remains unchanged. In crystals of class m vector $\boldsymbol{P}^{(0)}$ can change not only its magnitude, but also the direction, remaining however within the plane of symmetry.

Let us consider the influence of crystal symmetry on their dielectric susceptibility. The tensor of dielectric susceptibility, $\boldsymbol{\alpha}$, as any symmetric second-rank tensor, has three eigenvalues; if they are all different, the symmetry of the tensor is mmm, if two of them coincide, it is ∞/mm, if all three coincide, it is $\infty\ \infty\ m$.

Let us find out what crystals can have tensor $\boldsymbol{\alpha}$ with all the three eigenvalues different:

$$\boldsymbol{\alpha} = \alpha_{(1)}\boldsymbol{u}^{(1)}\boldsymbol{u}^{(1)} + \alpha_{(2)}\boldsymbol{u}^{(2)}\boldsymbol{u}^{(2)} + \alpha_{(3)}\boldsymbol{u}^{(3)}\boldsymbol{u}^{(3)}. \tag{27.1}$$

Point groups of the symmetry of such crystals are, according to Neumann's principle, either a subgroup of the mmm group or coin-

cide with the latter. This requirement is met by all crystals of the lower category, and by them alone.

Somewhat more complicated is a similar question for tensor $\boldsymbol{\alpha}$ with two of its eigenvalues coinciding:

$$\boldsymbol{\alpha} = \alpha_{\perp}\mathbf{I} + (\alpha_{\parallel} - \alpha_{\perp})\, \boldsymbol{kk}. \tag{27.2}$$

Point groups of the symmetry of crystals whose tensors of dielectric susceptibility have such a structure should be subgroups of the ∞/mm group. Such are the groups of crystals of the intermediate category and textures. In this case two of the eigenvalues of tensor $\boldsymbol{\alpha}$ always coincide. However, the point groups of crystals of the lower category are also subgroups of the ∞/mm group: although the dielectric susceptibility tensor of such crystals can have three different eigenvalues, the symmetry of the crystals permits the coincidence of two of them. Matter tensors, however, depend on the external conditions, for instance, on temperature. If in crystals of the lower category two eigenvalues of tensor $\boldsymbol{\alpha}$ coincide at a certain temperature, there are no reasons for both of them to change identically with a change in temperature: a matter tensor of such an irregularly high symmetry is not inherent in a given crystal in general, but only in the given crystal at strictly definite external conditions. This symmetry will be lost by the tensor under a slightest change of external conditions. Thus, in a general case, the tensor of dielectric susceptibility of any crystal of the lower category has symmetry mmm; and only for some crystals, and at strictly definite external conditions the symmetry rises to ∞/mm.

The tensor of dielectric permittivity $\boldsymbol{\varkappa}$ with three coinciding eigenvalues is

$$\boldsymbol{\varkappa} = \varkappa\mathbf{I} \tag{27.3}$$

and has symmetry $\infty\infty m$. Such tensors of dielectric permittivity belong to crystals whose symmetry point groups are the subgroups of group $\infty\infty m$, not being the subgroups of group ∞/mm. Such are the point groups of the crystals of the higher category. Isotropic and gyrotropic bodies also have a similar tensor of dielectric permittivity. The symmetry of the dielectric susceptibility tensor is of the same kind.

By substituting tensor $\boldsymbol{\alpha} = \alpha\mathbf{I}$ in relation (26.13) and noting that in all crystals of the higher category, in gyrotropic and isotropic bodies, the vector of spontaneous polarization is identically equal to zero, we find

$$\boldsymbol{P} = \alpha\mathbf{I}\cdot\boldsymbol{E} = \alpha\boldsymbol{E}. \tag{27.4}$$

Thus, the dependence of the polarization on the electric field intensity in crystals of the higher category is the same as in isotropic bodies—their dielectric susceptibility is isotropic.

Let us consider the orientation of the eigenvectors of the dielectric susceptibility tensor with respect to the crystal-physical system of coordinates. Since the crystals of the triclinic system have neither axes, nor planes of symmetry, the eigenvectors of tensor $\boldsymbol{\alpha}$ should not coincide with the mutually orthogonal unit vectors of the crystal-physical system of coordinates; even if under certain external conditions one of the eigenvectors coincides with one of the unit vectors a change in these conditions will, generally speaking, disturb the coincidence. Therefore in the crystal-physical coordinate system the tensor of the dielectric susceptibility of a crystal of the triclinic system has the form

$$\| \alpha_{ij} \| = \begin{Vmatrix} \alpha_{11} & \alpha_{12} & \alpha_{31} \\ \alpha_{12} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{23} & \alpha_{33} \end{Vmatrix}. \tag{27.5}$$

In crystals of the monoclinic system the unit vector $\boldsymbol{e}_2$ is directed along the 2-fold axis or along a perpendicular to the symmetry plane (see Table 4.1). Since the symmetry elements of the crystal are at the same time the symmetry elements of tensor $\boldsymbol{\alpha}$, $\boldsymbol{e}_2$ should coincide with one of the eigenvectors of tensor $\boldsymbol{\alpha}$, say, with $\boldsymbol{u}^{(2)}$. Thus, in the crystal-physical system of coordinates

$$\| \alpha_{ij} \| = \begin{Vmatrix} \alpha_{11} & 0 & \alpha_{31} \\ 0 & \alpha_{(2)} & 0 \\ \alpha_{31} & 0 & \alpha_{33} \end{Vmatrix}. \tag{27.6}$$

For the crystals of the rhombic system all mutually orthogonal unit vectors of the crystal-physical coordinate system are directed along the 2-fold symmetry axes or along the perpendiculars to symmetry planes. According to Neumann's principle, the dielectric susceptibility tensor has the same axes and symmetry planes, and therefore these unit vectors coincide (up to their sign) with the eigenvectors of the tensor. Consequently,

$$\| \alpha_{ij} \| = \begin{Vmatrix} \alpha_{(1)} & 0 & 0 \\ 0 & \alpha_{(2)} & 0 \\ 0 & 0 & \alpha_{(3)} \end{Vmatrix}. \tag{27.7}$$

It also follows from Neumann's principle that for crystals of the intermediate category and for textures the principal symmetry axis coincides with axis ∞ of the dielectric tensor; since it is directed along $\boldsymbol{e}_3$,

$$\| \alpha_{ij} \| = \begin{Vmatrix} \alpha_{\perp} & 0 & 0 \\ 0 & \alpha_{\perp} & 0 \\ 0 & 0 & \alpha_{\parallel} \end{Vmatrix}. \tag{27.8}$$

Finally, the dielectric susceptibility tensor for cubic crystals and isotropic bodies is the same in all Cartesian systems of coordinates, including of course the crystal-physical one:

$$\|\alpha_{ij}\| = \begin{Vmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{Vmatrix}. \tag{27.9}$$

The dielectric susceptibility tensor, as any matter tensor, depends on the external conditions. Its eigenvalues change with the changes in these conditions, but if the symmetry of the crystal calls for the coincidence of two or all three eigenvalues, they remain coincident even under the changed conditions. Unless their direction is determined by the symmetry of the crystal the orientation of the eigenvectors with respect to the crystal also changes with the change in the external conditions. In triclinic crystals a change in the orientation of the eigenvectors is in no way restricted by crystal's symmetry. In monoclinic crystals one eigenvector which is directed along a symmetry axis or along the perpendicular to a symmetry plane remains unmoved, while the other two rotate with a change in the external conditions, still remaining perpendicular to the first vector and to each other. In all the other crystals and in all textures the orientation of the dielectric susceptibility tensor is fully determined by symmetry and therefore does not change with the change of the external conditions.

We have discussed the influence of crystal symmetry on the dielectric susceptibility tensor $\boldsymbol{\alpha}$. The symmetry of crystals has exactly the same influence on all other symmetric second-rank tensors specifying the properties of crystals. However it is necessary to distinguish tensors describing other properties (for example, the thermal conductivity tensor $\boldsymbol{\lambda}$, see Sec. 33) and tensors describing the same property, tensor α, the dielectric permittivity tensor $\boldsymbol{\varkappa} = \mathbf{I} + 4\pi\boldsymbol{\alpha}$ and the dielectric impermeability tensor $\boldsymbol{\eta} = \boldsymbol{\varkappa}^{-1}$. All symmetric second-rank tensors describing the properties of triclinic and monoclinic crystals are referred to principal axes, but for tensors $\boldsymbol{\alpha}$, $\boldsymbol{\varkappa}$, $\boldsymbol{\eta}$ these axes coincide, while for tensor $\boldsymbol{\lambda}$ they are different; if in any crystal, at certain external conditions the symmetry of tensor $\boldsymbol{\alpha}$ is irregularly high, the symmetry of tensors $\boldsymbol{\varkappa}$ and $\boldsymbol{\eta}$ will also be as high, while the symmetry of tensor $\boldsymbol{\lambda}$ will be normal. This distinction is explained by the fact that the eigenvectors of tensors $\boldsymbol{\alpha}$, $\boldsymbol{\varkappa}$, $\boldsymbol{\eta}$ coincide and the eigenvalues are interrelated as

$$\varkappa_{(i)} = 1 + 4\pi\alpha_{(i)}, \quad \eta_i = 1/\varkappa_{(i)}, \tag{27.10}$$

while the eigenvectors of tensor $\boldsymbol{\lambda}$ coincide with the eigenvectors of tensor $\boldsymbol{\alpha}$ insofar as it is required by crystal symmetry, and the eigenvalues of the former tensor have no connection at all with the eigenvalues of tensor $\boldsymbol{\alpha}$.

Sec. 28. Crystals in a Uniform Electric Field

Capacitor with an Anisotropic Dielectric. Let us place a crystal slab, of area S and thickness d ($d \ll \sqrt{S}$) between the two condenser plates. Let us introduce a unit vector $\boldsymbol{n}$ of a perpendicular to the slab; its components in the crystal-physical system of coordinates are n_1, n_2, n_3. Assuming that the components of the dielectric permittivity tensor $\varkappa_{ij} = \boldsymbol{e}_i \cdot \boldsymbol{\varkappa} \cdot \boldsymbol{e}_j$ in the crystal-physical system of coordinates are known let us find the capacity of the condenser C ($\boldsymbol{n}$).

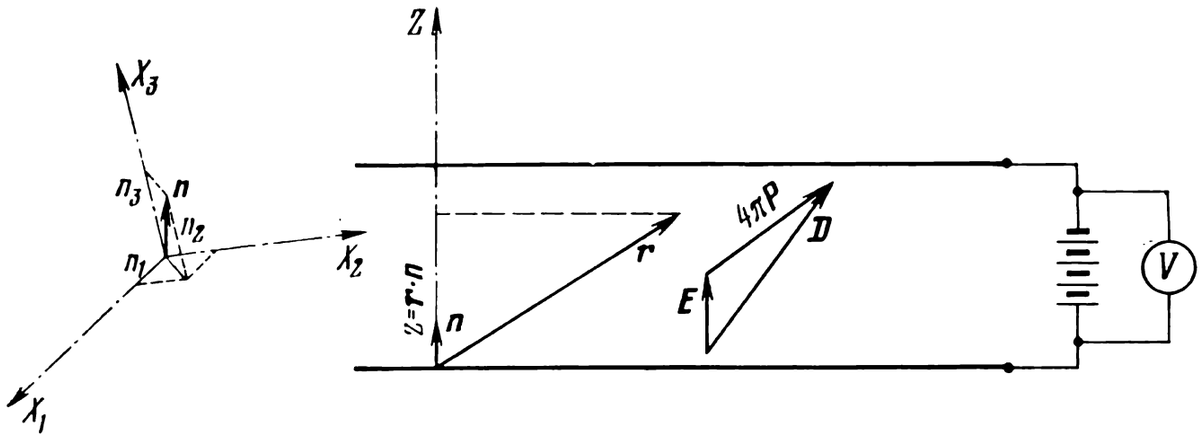


Fig. 28.1. Electric field vector, electric field induction vector and electric polarization in a plane capacitor with anisotropic dielectric

Since the slab area is much larger than the square of its thickness, we can neglect the distortion of the field near its edges and assume that potential φ varies only along the thickness of the slab. Let us choose a reference point on one of the slab surfaces (say, on the lower one, Fig. 28.1) and suppose that vector $\boldsymbol{n}$ is directed from the lower surface to the upper one. Then the distance between point $\boldsymbol{r}$ and the lower surface will be $z = \boldsymbol{r} \cdot \boldsymbol{n}$ and $\varphi = \varphi(z.)$ The intensity of the electric field

$$\boldsymbol{E} = -\operatorname{grad} \varphi = -\frac{d\varphi}{dz}\frac{dz}{d\boldsymbol{r}} = -\frac{d\varphi}{dz}\boldsymbol{n}. \tag{28.1}$$

Then the induction

$$\boldsymbol{D} = -\frac{d\varphi}{dz}\boldsymbol{\varkappa} \cdot \boldsymbol{n}, \quad D_i = -\frac{d\varphi}{dz}\varkappa_{ik} n_k \tag{28.2}$$

and equation div $\boldsymbol{D} = 0$ will be

$$\frac{\partial D_i}{\partial x_i} = -\frac{d^2\varphi}{dz^2} n_i \varkappa_{ik} n_k = 0, -\frac{d^2\varphi}{dz^2}\boldsymbol{n} \cdot \boldsymbol{\varkappa} \cdot \boldsymbol{n} = 0, \tag{28.3}$$

or simply $d^2\varphi/dz^2 = 0$. The general solution of this equation is $\varphi(z) = Az + B$. The potential difference between the plates is

$U = \varphi(0) - \varphi(d)$, so that

$$\varphi(z) = -\frac{U}{d} z + \varphi(0), \tag{28.4}$$

$$\boldsymbol{E} = \frac{U}{d} \boldsymbol{n}, \quad E_k = \frac{U}{d} n_k, \tag{28.5}$$

$$\boldsymbol{D} = \frac{U}{d} \boldsymbol{\varkappa} \cdot \boldsymbol{n} \quad D_i = \frac{U}{d} \varkappa_{ik} n_k. \tag{28.6}$$

The surface charge density at the lower plate $\rho_{\text{surf}} = (1/4\pi)\, \boldsymbol{n} \cdot \boldsymbol{D}$, and the total charge on the plate $Q = S\rho_{\text{surf}} = (SU/\pi d)\, \boldsymbol{n} \cdot \boldsymbol{\varkappa} \cdot \boldsymbol{n}$. Consequently, the capacity

$$C = Q/U = \frac{S}{4\pi d} \boldsymbol{n} \cdot \boldsymbol{\varkappa} \cdot \boldsymbol{n} = \frac{S}{4\pi d} \varkappa_{ik} n_i n_k. \tag{28.7}$$

If the obtained result is compared with the formula of the capacitance of the capacitor with an isotropic dielectic

$$C = \frac{S}{4\pi d} \varkappa, \tag{28.8}$$

it will be found that the role of dielectric permittivity $\varkappa$ is now played by $\boldsymbol{n} \cdot \boldsymbol{\varkappa} \cdot \boldsymbol{n} = \varkappa_{ik} n_i n_k$—the normal component of the dielectric permittivity tensor in the direction perpendicular to the plane of the slab, therefore $\boldsymbol{n} \cdot \boldsymbol{\varkappa} \cdot \boldsymbol{n}$ is sometimes called the dielectric permittivity of a crystal in direction $\boldsymbol{n}$. This does not mean, however, that for any other electrostatical problem for anisotropic media a correct answer can be obtained by substituting $\boldsymbol{n} \cdot \boldsymbol{\varkappa} \cdot \boldsymbol{n}$ for $\varkappa$ in the solution of a corresponding isotropic problem: in other cases quite different quantities play the role of dielectric permittivity in a given direction.

As was shown in Sec. 21, we can calculate all the components of a tensor when we know its six properly chosen normal components. Therefore, having measured the capacities of capacitors with six differently oriented slabs made of a certain crystal, we can calculate the dielectric permittivity tensor of the crystal, six slabs being actually required in this case only for triclinic crystals. For calculating the dielectric permittivity tensor for monoclinic crystals it will suffice to make such measurements with four slabs, for rhombic crystals, with three slabs, for crystals of intermediate systems and various textures, with two slabs, and finally, for cubic crystals because of the crystals' dielectric isotropy only with one arbitrarily oriented slab.

In some cases crystal symmetry permits essentially simplifying the calculation formula (28.7), see Table 28.1.

A Crystal with a Plane-parallel Interlayer in an Electric Field. Let us solve the following general problem: in an infinite anisotropic medium, characterized by the dielectric permittivity tensor $\boldsymbol{\varkappa}^{(e)}$, there is a plane-parallel interlayer of another anisotropic material with the dielectric permittivity tensor $\boldsymbol{\varkappa}^{(i)}$. As usually, we shall

Table 28.1

Normal Component $n \cdot \varkappa \cdot n$ of the Dielectric Permittivity Tensor $\varkappa$ Expressed in Terms of the Components of the Unit Vector n and in Terms of Miller Indices (hkl) of a Plane Perpendicular to n

Triclinic system, general equations

$$n \cdot \varkappa \cdot n = \varkappa_{ij} n_i n_j = \frac{\varkappa_{il} E_i^{\alpha} E_{jl}^{\beta} h_\alpha h_\beta}{g^{\gamma\delta} h_\gamma h_\delta}$$

Monoclinic system $(2 \parallel X_2,\ m \perp X_2)$

$$n \cdot \varkappa \cdot n = \varkappa_{11} n_1^2 + \varkappa_{22} n_2^2 + \varkappa_{33} n_3^2 + 2\varkappa_{31} n_3 n_1 =$$
$$= [h^2 b^2 c^2 \varkappa_{11} + k^2 c^2 a^2 \varkappa_{22} \sin^2 \beta + l^2 a^2 b^2 (\varkappa_{11} \cos^2 \beta + \varkappa_{33} \sin^2 \beta - \varkappa_{31} \sin 2\beta) -$$
$$- 2\, lhab^2 c\, (\varkappa_{11} \cos \beta - \varkappa_{31} \sin \beta)] / (h^2 b^2 c^2 + k^2 c^2 a^2 \sin^2 \beta + l^2 a^2 b^2 - 2lhab^2 c \cos \beta)$$

Rhombic system

$$n \cdot \varkappa \cdot n = \varkappa_{11} n_1^2 + \varkappa_{22} n_2^2 + \varkappa_{33} n_3^2 = \frac{h^2 b^2 c^2 \varkappa_{11} - k^2 c^2 a^2 \varkappa_{22} + l^2 a^2 b^2 \varkappa_{33}}{h^2 b^2 c^2 + k^2 c^2 a^2 + l^2 a^2 b^2}$$

Crystals of the intermediate category and textures

$$n \cdot \varkappa \cdot n = \varkappa_{11} (n_1^2 + n_2^2) + \varkappa_{33} n_3^2 = \varkappa_{11} + (\varkappa_{33} - \varkappa_{11})\, n_3^2$$

Tetragonal system

$$n \cdot \varkappa \cdot n = \frac{(h^2 + k^2)\, c^2 \varkappa_{11} + l^2 a^2 \varkappa_{33}}{(h^2 + k^2)\, c^2 + l^2 a^2}$$

Hexagonal and trigonal systems (in hexagonal orientation)

$$n \cdot \varkappa \cdot n = \frac{4\,(h^2 + k^2 + hk)\, c^2 \varkappa_{11} + 3 l^2 a^2 \varkappa_{33}}{4\,(h^2 + k^2 + hk)\, c^2 + 3 l^2 a^2}$$

Cubic system and isotropic bodies

$$n \cdot \varkappa \cdot n = \varkappa$$

Notation: h_α – Miller indices for a plane, E_i^{α} – matrix connecting mutually orthogonal unit vectors e_i of the crystal-physical coordinate system with base vectors a_α of the crystal lattice: $e_i = E_i^{\alpha} a_\alpha$; $g^{\gamma\delta}$ – contravariant components of the lattice metric tensor; a, b, c, β – cell parameters.

denote the unit vector of a perpendicular to the plane of the interlayer by $\boldsymbol{n}$. Let the electric field, $\boldsymbol{E}^{(e)}$, in the medium be uniform. Let us find the field $\boldsymbol{E}^{(i)}$ in the interlayer. It is natural to assume that this field is also uniform. Then the electrostatical differential equations will be identically satisfied, and only boundary conditions will remain to be taken care of. For vector $\boldsymbol{E}$ to satisfy the boundary conditions, it is necessary for vectors $\boldsymbol{E}^{(e)}$ and $\boldsymbol{E}^{(i)}$ to differ from each other by a vector parallel to normal $\boldsymbol{n}$:

$$\boldsymbol{E}^{(i)} = \boldsymbol{E}^{(e)} + A\boldsymbol{n}. \tag{28.9}$$

The unknown constant A is found from the boundary conditions for the induction vector. Induction in the medium is as follows

$$\boldsymbol{D}^{(e)} = \varkappa^{(e)} \cdot \boldsymbol{E}^{(e)}, \tag{28.10}$$

and in the interlayer it is

$$\boldsymbol{D}^{(i)} = \varkappa^{(i)} \cdot \boldsymbol{E}^{(i)} = \varkappa^{(i)} \cdot \boldsymbol{E}^{(e)} + A\varkappa^{(i)} \cdot \boldsymbol{n}. \tag{28.11}$$

The boundary conditions for $\boldsymbol{D}$ require that

$$\boldsymbol{n} \cdot \varkappa^{(i)} \cdot \boldsymbol{E}^{(e)} + A\boldsymbol{n} \cdot \varkappa^{(i)} \cdot \boldsymbol{n} = \boldsymbol{n} \cdot \varkappa^{(e)} \cdot \boldsymbol{E}^{(e)}, \tag{28.12}$$

whence we find

$$A = \frac{\boldsymbol{n} \cdot (\varkappa^{(e)} - \varkappa^{(i)}) \cdot \boldsymbol{E}^{(e)}}{\boldsymbol{n} \cdot \varkappa^{(i)} \cdot \boldsymbol{n}} \tag{28.13}$$

and finally

$$\boldsymbol{E}^{(i)} = \boldsymbol{E}^{(e)} + \frac{\boldsymbol{n} \cdot (\varkappa^{(e)} - \varkappa^{(i)}) \cdot \boldsymbol{E}^{(e)}}{\boldsymbol{n} \cdot \varkappa^{(i)} \cdot \boldsymbol{n}} \boldsymbol{n}, \tag{28.14}$$

$$E_j^{(i)} = [\delta_{jl} + (1/\varkappa_{pq}^{(i)} n_p n_q)\, n_j n_k\, (\varkappa_{kl}^{(e)} - \varkappa_{kl}^{(i)})]\, E_l^{(e)}.$$

If, in particular, the field in the medium is perpendicular to the interlayer plane, the field in the plane will also have this property and, as can be readily calculated,

$$\boldsymbol{E}^{(i)} = \frac{\boldsymbol{n} \cdot \varkappa^{e} \cdot \boldsymbol{n}}{\boldsymbol{n} \cdot \varkappa^{(i)} \cdot \boldsymbol{n}} E^{(e)} \boldsymbol{n} = \frac{\boldsymbol{n}\boldsymbol{n} \cdot \boldsymbol{D}^{(e)}}{\boldsymbol{n} \cdot \varkappa^{(i)} \cdot \boldsymbol{n}}. \tag{28.15}$$

Let us consider some important special cases which might be reduced to the problem discussed.

An Anisotropic Slab in a Uniform Electric Field. Substitute tensor $\mathbf{I}$ for $\varkappa^{(e)}$ in formula (28.14). We then find the field in it immediately:

$$\boldsymbol{E}^{(i)} = \boldsymbol{E}^{(e)} \quad \frac{\boldsymbol{n} \cdot (\varkappa^{(i)} - \mathbf{I}) \cdot \boldsymbol{E}^{(e)}}{\boldsymbol{n} \cdot \varkappa^{(i)} \cdot \boldsymbol{n}} \boldsymbol{n}. \tag{28.16}$$

In particular for, $\boldsymbol{E}^{(e)} = E^{(e)} \boldsymbol{n}$, we obtain

$$\boldsymbol{E}^{(i)} = \frac{1}{\boldsymbol{n} \cdot \varkappa^{(i)} \cdot \boldsymbol{n}} E^{(e)} \boldsymbol{n}. \tag{28.17}$$

A Plane-parallel Gap in an Infinite Anisotropic Medium. In this case $\varkappa^{(i)} = \mathbf{I}$. The field in the gap is

$$E^{(i)} = E^{(e)} + [n\cdot(\varkappa^{(e)} - \mathbf{I})\cdot E^{(e)}]\cdot n. \tag{28.18}$$

In an isotropic body for $E^{(e)} \parallel n$ the vector of the field intensity in the gap is equal to the electric induction vector of the body: $E^{(i)} = D^{(e)}$. For an anisotropic body this equality holds only if n is the eigenvector of tensor $\varkappa^{(e)}$, and in a general case vector $E^{(i)} = nn\cdot D^{(e)}$ is equal to the component of the induction vector in a body directed along n. This vector does not coincide with vector $D^{(e)}$ either in magnitude or in direction.

When vector $E^{(e)}$ is parallel to the gap ($n\cdot E^{(e)} = 0$), the field intensity of an isotropic body is equal to the field intensity of the gap, while in an anisotropic body

$$E^{(i)} = E^{(e)} + nn\cdot D^{(e)}. \tag{28.19}$$

The second term vanishes only under the condition that vector n is perpendicular not only to vector $E^{(e)}$ but also to vector $D^{(e)}$, in particular, when n is one of the eigenvectors of tensor $\varkappa^{(e)}$.

An Anisotropic Sphere in an Electric Field. Let an anisotropic sphere of radius R and with dielectric permittivity tensor $\varkappa$ be in an electric field, whose intensity away from the sphere is $E^{(0)}$. It is necessary to determine the electric field within and outside the sphere.

In an electric field the sphere is polarized and thus generates an additional field in its surroundings. Assuming that it coincides with the dipole field and that the dipole moment of the sphere is linearly related to $E^{(0)}$:

$$M = R^3\gamma\cdot E^{(0)}, \tag{28.20}$$

where tensor γ depends on $\varkappa$ but not on the direction of dimensionality vector $E^{(0)}$, and factor R^3 has been introduced for the dimensionality considerations. Then the field potential outside the sphere is

$$\varphi^{(e)} = -r\cdot E^{(0)} + (R/r)^3 r\cdot\gamma\cdot E^{(0)}. \tag{28.21}$$

Assume also that the field within the sphere is uniform and depends linearly on $E^{(0)}$; its potential will be

$$\varphi^{(i)} = -r\cdot\beta\cdot E^{(0)}, \tag{28.22}$$

where tensor β, as well as γ, depend only on $\varkappa$, but not on the direction of vector $E^{(0)}$. Potentials $\varphi^{(e)}$ and $\varphi^{(i)}$ satisfy the equations of electrostatics, while boundary conditions allow finding tensors β and γ. Thus, from the condition of continuity of the potential at the interface, it follows that

$$-R\cdot\beta\cdot E^{(0)} = -R\cdot E^{(0)} + R\cdot\gamma\cdot E^{(0)},$$

where $\boldsymbol{R}$ is the radius-vector of a point on the surface of the sphere. Replacing the scalar product $\boldsymbol{R}\cdot\boldsymbol{E}^{(0)}$ by an equal expression $\boldsymbol{R}\cdot\boldsymbol{I}\cdot\boldsymbol{E}^{(0)}$ and transferring all the terms to one side we obtain

$$\boldsymbol{R}\,(\gamma + \beta - \mathrm{I})\cdot\boldsymbol{E}^{(0)} = 0.$$

Insofar as this equality remains valid for all the possible directions of vectors $\boldsymbol{R}$ and $\boldsymbol{E}^{(0)}$, the tensor in round brackets is zero, i.e.

$$\beta + \gamma = \mathrm{I}. \tag{28.23}$$

From the continuity of the normal components of the electric induction vector at the interface it follows that

$$-\boldsymbol{R}\cdot\varkappa\cdot\beta\cdot\boldsymbol{E}^{(0)} = -2\boldsymbol{R}\cdot\gamma\cdot\boldsymbol{E}^{(0)} - \boldsymbol{R}\cdot\boldsymbol{E}^{(0)}.$$

Hence, we obtain in the same way

$$\varkappa\cdot\beta - 2\gamma = \mathrm{I}. \tag{28.24}$$

The solution of a system of two equations (28.23) and (28.24) linear with respect to tensors β and γ, is as follows

$$\beta = 3\,(\varkappa + 2\mathrm{I})^{-1},\quad \gamma = (\varkappa - \mathrm{I})\cdot(\varkappa + 2\mathrm{I})^{-1}. \tag{28.25}$$

Now we can readily write out the fields, both beyond and within the sphere, but we are mainly concerned with the latter one. Its intensity is

$$\boldsymbol{E}^{(i)} = 3\,(\varkappa + 2\mathrm{I})^{-1}\cdot\boldsymbol{E}^{(0)}, \tag{28.26}$$

while the induction satisfies a peculiar relation

$$\boldsymbol{D}^{(i)} = 3\boldsymbol{E}^{(0)} - 2\boldsymbol{E}^{(i)}, \tag{28.27}$$

which is derived by means of the following sequence of equalities:

$$\begin{aligned}\boldsymbol{D}^{(i)} = \varkappa\cdot\boldsymbol{E}^{(i)} &= 3\varkappa\cdot(\varkappa + 2\mathrm{I})^{-1}\cdot\boldsymbol{E}^{(0)} = \\ &= 3\,[(\varkappa + 2\mathrm{I}) - 2\mathrm{I}]\cdot(\varkappa + 2\mathrm{I})^{-1}\cdot\boldsymbol{E}^{(0)} = \\ &= [3\mathrm{I} - 6\,(\varkappa + 2\mathrm{I})^{-1}]\cdot\boldsymbol{E}^{(0)} = 3\boldsymbol{E}^{(0)} - 2\boldsymbol{E}^{(i)}.\end{aligned}$$

Sec. 29. The Field in a Spherical Gap in an Anisotropic Medium

In the preceding section we obtained a comparatively simple solution in a case of an anisotropic sphere in vacuum and a uniform field at a large distance from it. A seemingly similar problem of a spherical gap in an infinite anisotropic medium and a uniform field $\boldsymbol{E}^{(0)}$ at a large distance from it, is actually much more complicated. We shall give its solution without its proof, bearing in mind the importance of this problem for the microscopic theory of the crystal lattice *. It appears that the field in gap $\boldsymbol{E}^{(i)}$ is in this case also uniform, but its dependence on $\boldsymbol{E}^{(0)}$, even though still linear, is much more complicated.

Prior to writing out the solution of the problem let us consider, on the basis of the Curie principle, tensor S — a function of a symmetric second-rank ten-

* See the derivation in Landau and Lifshits (1957, Secs. 4, 8, 13). On the application of this problem to the microscopic theory of the crystal lattice s e Born and Huang Kun (1966) and Kittel (1975).

sor T. As was mentioned in Sec. 22, a symmetric second-rank tensor T is in any case invariant with respect to group *mmm*. It follows from the Curie principle that tensor S is invariant at least with respect to the same group. But since the tensor eigenvectors are directed along the symmetry axes of the tensor, it follows that the eigenvectors of the tensor-function coincide with the eigenvectors of the tensor-argument*. Hence it is evident that all tensors which are functions of a symmetric second-rank tensor might be reduced to a diagonal form in the same system of coordinates as the tensor-argument. It is said that $S = f(T)$ if in this system

$$\| S_{ik} \| = \begin{Vmatrix} S_{(1)} & 0 & 0 \\ 0 & S_{(2)} & 0 \\ 0 & 0 & S_{(3)} \end{Vmatrix} = \begin{Vmatrix} f(T_{(1)}) & 0 & 0 \\ 0 & f(T_{(2)}) & 0 \\ 0 & 0 & f(T_{(3)}) \end{Vmatrix}.$$

In particular, $S = \sqrt{T}$, if $S_{(i)} = \sqrt{T_{(i)}}$. Even functionals of tensors can be regarded this way; it is only necessary that the tensor-function proper system of coordinates remains unchanged throughout the whole range of changes of the tensor.

Let us now return to the problem posed at the beginning of this Section. Let $\varkappa$ be the tensor of dielectric permittivity coefficients of the anisotropic medium, and $\eta = \varkappa^{-1}$ be the tensor of the dielectric impermeability coefficients of the medium. We introduce tensors $\mu = \sqrt{\varkappa}$ and $\nu = \sqrt{\eta}$, as well as the *tensor of the depolarization coefficients*

$$\mathbf{N} = \frac{1}{2}\sqrt{\det \eta} \int_0^\infty \frac{(\eta + z\mathbf{I})^{-1}\, dz}{\sqrt{\det(\eta + z\mathbf{I})}}. \tag{29.1}$$

Then the field in the gap $E^{(i)}$ is uniform and depends on the field away from the gap $E^{(0)}$ as follows:

$$E^{(i)} = [\mathbf{I} - \nu \cdot \mathbf{N} \cdot (\mathbf{I} - \eta) \cdot \mu]^{-1} \cdot E^{(0)}. \tag{29.2}$$

In the proper system of coordinates formulas (29.1) and (29.2) are essentially simplified. The eigenvalues of tensors μ and ν are omitted from (29.2) (they are simply cancelled out) and it yields

$$E_k^{(i)} = \frac{E_k^{(0)}}{1 - N_{(k)}(1 - \eta_{(k)})}. \tag{29.3}$$

For the eigenvalues of the tensor of the depolarization coefficients we obtain from (29.1)

$$N_{(k)} = \frac{1}{2}\sqrt{\det \eta} \int_0^\infty \frac{dz}{(\eta_{(k)} + z)\sqrt{\det(\eta + z\mathbf{I})}}. \tag{29.4}$$

* Moreover, it follows from the Curie principle that the tensor-function is symmetric with respect to indices, if the tensor-argument has this property. The point is that if a second-rank tensor is essentially asymmetric with respect to indices, i.e. is not equal to a tensor transposed with respect to it, some of the operations of group *mmm* are sure to be absent from its symmetry group.

The integral in this formula is elliptic; it is expressed in terms of well-known elliptic integrals of the first and second kind $F(\varphi, k)$ and $E(\varphi, k)$ *. Namely assuming that $\eta_{(1)} > \eta_{(2)} > \eta_{(3)}$ and denoting

$$\varphi = \arcsin \sqrt{\frac{\eta_{(1)} - \eta_{(3)}}{\eta_{(1)}}}, \quad k = \sqrt{\frac{\eta_{(1)} - \eta_{(2)}}{\eta_{(1)} - \eta_{(3)}}},$$

we have

$$N_{(1)} = \frac{\sqrt{\eta_{(1)}\eta_{(2)}\eta_{(3)}}}{(\eta_{(1)} - \eta_{(2)})\sqrt{\eta_{(1)} - \eta_{(3)}}} [F(\varphi, k) - E(\varphi, k)], \tag{29.5a}$$

$$N_{(2)} = \frac{\sqrt{\eta_{(1)}\eta_{(2)}\eta_{(3)}}}{\eta_{(1)} - \eta_{(2)}} \left[\frac{\sqrt{\eta_{(1)} - \eta_{(3)}}}{\eta_{(2)} - \eta_{(3)}} E(\varphi, k) - \right.$$

$$\left. - \frac{1}{\sqrt{\eta_{(1)} - \eta_{(3)}}} F(\varphi, k) \right] - \frac{\eta_{(3)}}{\eta_{(2)} - \eta_{(3)}}, \tag{29.5b}$$

$$N_{(3)} = \frac{\eta_{(2)}}{\eta_{(2)} - \eta_{(3)}} - \frac{\sqrt{\eta_{(1)}\eta_{(2)}\eta_{(3)}}}{(\eta_{(2)} - \eta_{(3)})\sqrt{\eta_{(1)} - \eta_{(3)}}} E(\varphi, k). \tag{29.5c}$$

Summing up the eigenvalues of the tensor of depolarization coefficients we obtain

$$N_{ii} = 1. \tag{29.6}$$

For crystals of the intermediate category, when two eigenvalues of the tensor of dielectric impermeability coefficients coincide, the integrals in (29.5) are expressed in terms of elementary functions. Two cases should be distinguished here. If $\eta_{\parallel} > \eta_{\perp}$ then, denoting

$$e = \sin \varphi = \sqrt{\frac{\eta_{\parallel} - \eta_{\perp}}{\eta_{\parallel}}},$$

we obtain

$$N_{\parallel} = 1 - \frac{1}{2e^3}\left[2e - (1 - e^2)\ln\frac{1+e}{1-e}\right],$$
$$N_{\perp} = \frac{1}{4e^3}\left[2e - (1 - e^2)\ln\frac{1+e}{1-e}\right] \tag{29.7}$$

But if $\eta_{\perp} > \eta_{\parallel}$, we denote

$$f = \sqrt{\frac{\eta_{\perp} - \eta_{\parallel}}{\eta_{\parallel}}},$$

---

* By definition, the elliptic integral of the first kind is

$$F(\varphi, k) = \int_0^{\varphi} \frac{1}{\sqrt{1 - k^2 \sin^2 \psi}} d\psi,$$

while the elliptic integral of the second kind is

$$E(\varphi, k) = \int_0^{\varphi} \sqrt{1 - k^2 \sin^2 \psi}\, d\psi.$$

The values of these integrals in terms of φ and k are given in many handbooks of mathematical tables, see, e.g. Jahnke, Emde and Lesch (1933).

and then

$$N_{\parallel}=1-\frac{1}{f^3}(\arctan f-f),\quad N_{\perp}=\frac{1}{2f^3}(\arctan f-f). \tag{29.8}$$

Formulas (29.7) and (29.8) can be simplified if the anisotropy of the dielectric properties of the crystal is small. Namely, if $e \ll 1$, formulas (29.7) can be approximately written as

$$N_{\parallel}=\frac{1}{3}-\frac{2}{15}e^2,\quad N_{\perp}=\frac{1}{3}+\frac{1}{15}e^2, \tag{29.9}$$

while formulas (29.8) when $f \ll 1$, are written as

$$N_{\parallel}=\frac{1}{3}+\frac{2}{15}f^2,\quad N_{\perp}=\frac{1}{3}-\frac{1}{15}f^2. \tag{29.10}$$

For the crystals of the cubic system and for isotropic bodies we obtain from (29.6)

$$N=\frac{1}{3}N_{ii}=\frac{1}{3}. \tag{29.11}$$

Now, using relation (29.2), we find

$$E^{(1)}=\frac{3\varkappa}{2\varkappa+1}E^{(0)}; \tag{29.12}$$

this well-known result could certainly be obtained in a very simple way.

Sec. 30. Fields of a Point Charge and a Dipole in an Anisotropic Medium

Let us consider a field of point charge e in an anisotropic medium characterized by the dielectric permittivity tensor $\varkappa$. The density function of electric charges $\rho(\boldsymbol{r})$ for a point charge is known to be reduced to the Dirac δ-function multiplied by the magnitude of the charge: $\rho(\boldsymbol{r})=e\delta(\boldsymbol{r}-\boldsymbol{r}^0)$ where vector $\boldsymbol{r}^{(0)}$ determines the location of the charge. Placing the charge in the origin of the system of coordinates, we obtain

$$\operatorname{div}\boldsymbol{D}=4\pi e\delta(\boldsymbol{r}). \tag{30.1}$$

Since $\boldsymbol{D}=-\varkappa\cdot\operatorname{grad}\varphi$ and tensor $\varkappa$ does not depend on the coordinates, it follows from (30.1) that potential φ satisfies equation

$$\varkappa_{ij}\frac{\partial^2\varphi}{\partial x_i\,\partial x_j}=-4\pi e\delta(\boldsymbol{r}). \tag{30.2}$$

We write it in the system of coordinates X_1, X_2, X_3 constructed on the eigenvectors of tensor $\varkappa$:

$$\varkappa_{(1)}\frac{\partial^2\varphi}{\partial x_1^2}+\varkappa_{(2)}\frac{\partial^2\varphi}{\partial x_2^2}+\varkappa_{(3)}\frac{\partial^2\varphi}{\partial x_3^2}=-4\pi e\delta(x_1)\,\delta(x_2)\,\delta(x_3). \tag{30.3}$$

To solve equation (30.3) we change our variables: instead of variables x_i we introduce variables $y_i=x_i/\sqrt{\varkappa_{(i)}}$. Using formula $\delta(\varkappa^{1/2}y)=\varkappa^{-1/2}\delta(y)$ for the transformation of the δ-functions we obtain

from (30.3)

$$\frac{\partial^2\varphi}{\partial y_1^2}+\frac{\partial^2\varphi}{\partial y_2^2}+\frac{\partial^2\varphi}{\partial y_3^2}=-\frac{4\pi e}{\sqrt{\varkappa_{(1)}\varkappa_{(2)}\varkappa_{(3)}}}\,\delta(y_1)\,\delta(y_2)\,\delta(y_3). \tag{30.4}$$

This equation determines the potential of a point charge field $e' = e/\sqrt{\varkappa_{(1)}\varkappa_{(2)}\varkappa_{(3)}}$ in vacuum; its solution is $\varphi = e'/\sqrt{y_1^2+y_2^2+y_3^2}$, or, returning to former variables,

$$\varphi=\frac{e}{\sqrt{\varkappa_{(1)}\varkappa_{(2)}\varkappa_{(3)}}}\left(\frac{x_1^2}{\varkappa_{(1)}}+\frac{x_2^2}{\varkappa_{(2)}}+\frac{x_3^2}{\varkappa_{(3)}}\right)^{-1/2}.$$

We introduce into our consideration the dielectric impermeability tensor $\boldsymbol{\eta} = \boldsymbol{\varkappa}^{-1}$. Noting that $\varkappa_{(1)}\varkappa_{(2)}\varkappa_{(3)} = \det\boldsymbol{\varkappa} = 1/\det\boldsymbol{\eta}$, and

$$\frac{x_1^2}{\varkappa_{(1)}}+\frac{x_2^2}{\varkappa_{(2)}}+\frac{x_3^2}{\varkappa_{(3)}}=\eta_{(1)}x_1^2+\eta_{(2)}x_2^2+\eta_{(3)}x_3^2=\boldsymbol{r}\cdot\boldsymbol{\eta}\cdot\boldsymbol{r},$$

we write the potential of the field of the electric point charge e in an anisotropic medium in a non-coordinate form:

$$\varphi=e\sqrt{\frac{\det\boldsymbol{\eta}}{\boldsymbol{r}\cdot\boldsymbol{\eta}\cdot\boldsymbol{r}}}. \tag{30.5}$$

Equation $\varphi(\boldsymbol{r}) = \text{const}$ determines equipotential surfaces. From (30.5) it follows that these are ellipsoids

$$\boldsymbol{r}\cdot\boldsymbol{\eta}\cdot\boldsymbol{r}=\text{const} \tag{30.6}$$

i.e. the characteristic surfaces (indicatrices) of the dielectric impermeability tensor $\boldsymbol{\eta}$ (see Sec. 22).

Representing the radius-vector $\boldsymbol{r}$ as $\boldsymbol{r} = r\boldsymbol{p}$, where r is the distance from the origin, and $\boldsymbol{p}$ is the unit vector of a beam, we can write

$$\varphi=e\sqrt{\frac{\det\boldsymbol{\eta}}{\boldsymbol{p}\cdot\boldsymbol{\eta}\cdot\boldsymbol{p}}}\,\frac{1}{r} \tag{30.7}$$

instead of (30.5).

A comparison of this formula with a similar one for the isotropic medium $\varphi = e/(\varkappa r)$ shows that the role of "dielectric permittivity in the direction of the unit vector $\boldsymbol{p}$" is played here by the quantity

$$\varkappa^{\varphi}(\boldsymbol{p})=\sqrt{\frac{\boldsymbol{p}\cdot\boldsymbol{\eta}\cdot\boldsymbol{p}}{\det\boldsymbol{\eta}}}. \tag{30.8}$$

Knowing the potential, it is easy to find the intensity

$$\boldsymbol{E}=-\operatorname{grad}\varphi=\frac{e\sqrt{\det\boldsymbol{\eta}}}{(\boldsymbol{r}\cdot\boldsymbol{\eta}\cdot\boldsymbol{r})^{3/2}}\,\boldsymbol{\eta}\cdot\boldsymbol{r} \tag{30.9}$$

and the induction of the electric field

$$\boldsymbol{D}=\boldsymbol{\varkappa}\cdot\boldsymbol{E}=\frac{e\sqrt{\det\boldsymbol{\eta}}}{(\boldsymbol{r}\cdot\boldsymbol{\eta}\cdot\boldsymbol{r})^{3/2}}\,\boldsymbol{r}; \tag{30.10}$$

in calculating the induction use was made of the fact that tensors $\boldsymbol{\eta}$ and $\boldsymbol{\varkappa}$ are mutually reciprocal.

Vectors of electric induction D in an anisotropic medium, as well as in an isotropic one, are directed along beams radiating from the charge, while the vectors of the electric field intensity E in an anisotropic medium, generally speaking, diverge from these beams. At the same time the absolute value of the field intensity decreases along each such beam, according to the same law $E(r) \sim 1/r^2$ as for the isotropic medium:

$$E = \frac{e\sqrt{p\cdot\eta\cdot\eta\cdot p \det\eta}}{(p\cdot\eta\cdot p)^{3/2}}\frac{1}{r^2}. \tag{30.11}$$

A comparison of this formula with a similar one for the isotropic medium $E = e/(\varkappa r^2)$ permits introducing one more "dielectric permittivity in the direction of unit vector p":

$$\varkappa^{(E)}(p) = \sqrt{\frac{(p\cdot\eta\cdot p)^3}{p\cdot\eta\cdot\eta\cdot p \det\eta}}. \tag{30.12}$$

Thus it is possible to introduce a great variety of definitions for "dielectric permittivity in a given direction"; therefore it is necessary to point out distinctly what particular quantity is meant in each individual case.

A natural generalization of the problem of a point charge field is the problem of a dipole field. Let us discuss a system of point charges e_n situated at points $r^{(n)}$. The field potential of such a system is equal to the sum of potentials of individual point charges, i.e.

$$\varphi(r) = \sum_n e_n \sqrt{\frac{\det\eta}{(r-r^{(n)})\cdot\eta\cdot(r-r^{(n)})}}. \tag{30.13}$$

Let us examine the field at a large distance from the charges. It can be conveniently assumed that a reference point is chosen somewhere near the charges, so that the remoteness of the observation point from the charges means that $r \gg r^{(n)}$. Let us expand (30.13) in a series restricting ourselves to the first two terms. Since

$$(r-r^{(n)})\cdot\eta\cdot(r-r^{(n)}) \approx r\cdot\eta\cdot r - r^{(n)}\cdot\eta\cdot r - r\cdot\eta\cdot r^{(n)} = \\ = r\cdot\eta\cdot r\left(1 - \frac{2r^{(n)}\cdot\eta\cdot r}{r\cdot\eta\cdot r}\right)$$

(utilizing the symmetry of tensor η), and approximate equalities $1/\sqrt{1-2\varepsilon} \approx 1/(1-\varepsilon) \approx 1+\varepsilon$ are valid for $\varepsilon \ll 1$, we obtain from (30.13)

$$\varphi(r) = \sqrt{\frac{\det\eta}{r\cdot\eta\cdot r}}\sum_n e_n\left(1 + \frac{r^{(n)}\cdot\eta\cdot r}{r\cdot\eta\cdot r} + \ldots\right). \tag{30.14}$$

The first term of this series is the potential of the field generated by the total charge $e = \sum_n e_n$. We are concerned with the field of the

system of charges which is neutral on the whole, when $e = 0$, and the next term of the series differs from zero. Then the field is determined mainly by the dipole couple

$$M = \sum_n e_n r^{(n)} \tag{30.15}$$

of the system of charges and its potential

$$\varphi(r) = \sqrt{\det \eta}\, \frac{M \cdot \eta \cdot r}{(r \cdot \eta \cdot r)^{3/2}}. \tag{30.16}$$

The field intensity

$$E(r) = -\operatorname{grad} \varphi = \sqrt{\det \eta}\, \frac{(M \cdot \eta \cdot r)\, \eta \cdot r - (r \cdot \eta \cdot r)\, \eta \cdot M}{(r \cdot \eta \cdot r)^{5/2}}, \tag{30.17}$$

and induction

$$D(r) = \varkappa \cdot E = \sqrt{\det \eta}\, \frac{3\,(M \cdot \eta \cdot r)\, r - (r \cdot \eta \cdot r)\, M}{(r \cdot \eta \cdot r)^{5/2}}. \tag{30.18}$$

For distinguishing in these formulas the role of the direction and the distance between the point of observation and the dipole we shall again use the unit vector of the beam p:

$$\varphi = \sqrt{\det \eta}\, \frac{M \cdot \eta \cdot p}{(p \cdot \eta \cdot p)^{3/2}}\, \frac{1}{r^2}, \tag{30.19}$$

$$E = \sqrt{\det \eta}\, \frac{3\,(M \cdot \eta \cdot p)\, \eta \cdot p - (p \cdot \eta \cdot p)\, \eta \cdot M}{(p \cdot \eta \cdot p)^{5/2}}\, \frac{1}{r^3}, \tag{30.20}$$

$$D = \sqrt{\det \eta}\, \frac{3\,(M \cdot \eta \cdot p)\, p - (p \cdot \eta \cdot p)\, M}{(p \cdot \eta \cdot p)^{5/2}}\, \frac{1}{r^3}. \tag{30.21}$$

In an isotropic medium the only plane among the equipotential surfaces is the plane passing through the dipole perpendicular to the vector of the dipole moment M. In an anisotropic medium a similar role is played by the plane also passing through the dipole, but perpendicular not to vector M but to vector $\eta \cdot M$. In an isotropic medium at all the points on the dipole axis ($p \parallel M$) vectors E and D are directed along one and the same axis ($E \parallel D \parallel M$). In an anisotropic medium only vector D is directed at such points along the dipole axis, while vector E is parallel to vector $\eta \cdot M$. The decrease in the potential and in the absolute values of field vectors with the increase of the distance from the dipole along any beam is the same in an anisotropic medium as in an isotropic one: the potential drops as $1/r^2$, the intensity and induction as $1/r^3$.

Sec. 31. Pyroelectrics

Pyroelectrics are crystals characterized by the non-zero vector of spontaneous polarization $P^{(0)}$, or spontaneous $D^{(0)} = 4\pi P^{(0)}$. The material equation of electrostatics for pyroelectric crystals

$$D = D^{(0)} + \varkappa \cdot E \tag{31.1}$$

combined with classical electrostatical equations and boundary conditions allows to study the behaviour of these crystals in the absence of external fields. Let us consider, for instance, a sphere of radius R made of a pyroelectric crystal; use in this case, as in the problem concerning a crystal sphere in Sec. 28, indefinite tensors β and γ that depend only on $\varkappa$. It would naturally be expected that the dipole moment of the sphere is

$$\boldsymbol{M} = R^3 \boldsymbol{\gamma} \cdot \boldsymbol{D}^{(0)}; \tag{31.2}$$

the field beyond the sphere is determined by this dipole moment so that its potential

$$\varphi^{(e)} = (R/r)^3 \, \boldsymbol{r} \cdot \boldsymbol{\gamma} \cdot \boldsymbol{D}^{(0)}, \tag{31.3}$$

and the field within the sphere is uniform:

$$\varphi^{(i)} = - \boldsymbol{r} \cdot \boldsymbol{\beta} \cdot \boldsymbol{D}^{(0)}. \tag{31.4}$$

We obtain from boundary conditions

$$\boldsymbol{R} \cdot (\boldsymbol{\beta} + \boldsymbol{\gamma}) \cdot \boldsymbol{D}^{(0)} = 0, \tag{31.5}$$

$$\boldsymbol{R} \cdot (\varkappa \boldsymbol{\beta} - 2\boldsymbol{\gamma} + \mathbf{I}) \cdot \boldsymbol{D}^{(0)} = 0, \tag{31.6}$$

where $\boldsymbol{R}$ is the radius-vector of an arbitrary point on the surface of the sphere. The solution of this electrostatic problem would not change if, prior to the experiment, we could arbitrarily impart to the crystal any spontaneous induction $\boldsymbol{D}^{(0)}$ chosen beforehand without changing the crystal's dielectric permittivity $\varkappa$ and, consequently, tensors β and γ. Therefore, the directions of vectors $\boldsymbol{R}$ and $\boldsymbol{D}^{(0)}$ can be considered arbitrary, and it is possible to pass from equalities (31.5) and (31.6) to tensor equations

$$\boldsymbol{\beta} + \boldsymbol{\gamma} = 0, \quad \varkappa \cdot \boldsymbol{\beta} - 2\boldsymbol{\gamma} + \mathbf{I} = 0.$$

Solving them, we obtain

$$\boldsymbol{\gamma} = - \boldsymbol{\beta} = (\varkappa + 2\mathbf{I})^{-1}. \tag{31.7}$$

Thus, a field is formed around the pyroelectric with the intensity

$$\boldsymbol{E}^{(e)} = - \operatorname{grad} \varphi^{(e)} = (R^3/r^5)\,(3\boldsymbol{rr} - r^2\mathbf{I})\,(\varkappa + 2\mathbf{I})^{-1} \cdot \boldsymbol{D}^{(0)}, \tag{31.8}$$

which decreases with the increase of the distance from the crystal as $1/r^3$. Within the crystal there develops a uniform field with intensity

$$\boldsymbol{E}^{(i)} = - (\varkappa + 2\mathbf{I})^{-1} \cdot \boldsymbol{D}^{(0)} \tag{31.9}$$

and induction

$$\boldsymbol{D}^{(i)} = \boldsymbol{D}^{(0)} + \varkappa \cdot \boldsymbol{E}^{(i)} = - (\varkappa + 2\mathbf{I}) \cdot \boldsymbol{E}^{(i)} + \varkappa \cdot \boldsymbol{E}^{(i)} = \\ = - 2\boldsymbol{E}^{(i)}, \tag{31.10}$$

which, as it can be seen, is not equal to spontaneous displacement. The fields of the induction and intensity vectors are shown in Fig. 31.1.

Pyroelectric crystals of other shapes apparently behave similarly in the absence of an external field. The field within them will no longer be uniform, but it is important that, as a rule, it differs from zero. They also generate a field around themselves, this field coincides with the dipole field only at distances considerably exceeding the linear dimensions of the crystals, while near the crystal it is more or less distorted—depending on the shape of the crystal. But the presence of fields both outside and inside a crystal is a common feature of all pyroelectric crystals regardless of their shape.

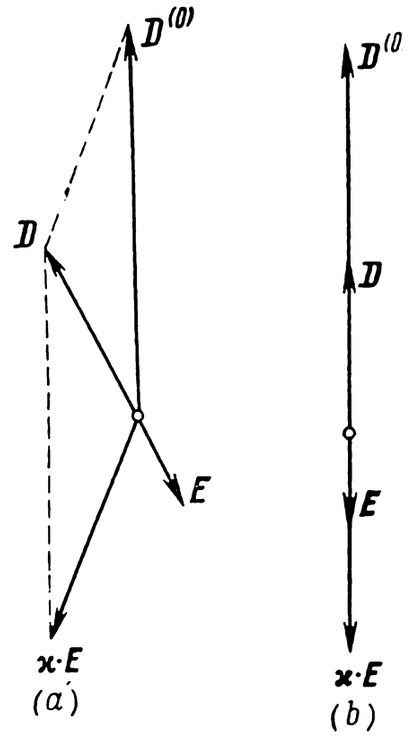


Fig. 31.1. Mutual array of the vectors of spontaneous induction and of the electric field intensity in a pyroelectric crystal sphere of class 1 or m (a) and of any of the other pyroelectric classes (b)

It is evident, however, that the real conditions of the life of crystals exclude the possibility of infinitely long existence of such fields. All dielectrics possess non-zero conductivity, even if sometimes very small, and therefore there occurs slow charge transfer in the crystal; the field of the charges that transferred to the boundary will oppose the fields both inside and outside the crystal. Moreover, there are always some ions in the air; under the action of the field outside the crystal they will, depending on the sign of the charge, be attracted to some part of the crystal surface and their fields will also oppose the field of the crystal and eventually balance it.

Therefore, the pyroelectric properties of crystals are observed and measured by sufficiently rapid changes of their temperature, since spontaneous polarization depends on temperature. Hence the very name of the phenomenon—pyroelectricity ("pyros" is Greek for fire). Thus, not the spontaneous polarization itself, but only its variations with temperature are measured. In the first approximation they are linear:

$$\boldsymbol{P}^{(0)}(T) - \boldsymbol{P}^{(0)}(T_0) = \boldsymbol{p}(T - T_0). \qquad (31.11)$$

Vector $\boldsymbol{p}$ is called the *vector of pyroelectric coefficients*. However, the principal feature of a pyroelectric, which determines the possibility of its utilization in practice, is the *pyroelectric figure of merit* $p/\varkappa$

equal to the ratio of the absolute value of the pyroelectric coefficient p to the normal component of the dielectric permittivity tensor in the direction of the pyroelectric axis $\varkappa = \boldsymbol{p}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{p}/p^2$.

Practical utilization of the pyroelectric effect became possible only a few years ago, when the industrial production of crystals (mainly ferroelectrics)* with pyroelectric coefficients of large values was started. The first place here belongs to lithium sulphate and lithium selenate whose pyroelectric coefficient magnitude is by an order higher than that of all the previously known pyroelectrics. The disadvantage of new pyroelectrics is the great dependence of their pyroelectric coefficient on temperature and consequent instability of the pyroeffect. Some textures, especially ceramics made of barium titanate, also have considerable pyroeffect.

Pyroelectric crystals are used in electrical thermometers which permit measuring temperature up to 10^{-6} K, as well as in the production of sensitive detectors of rapidly varying heat flows, in particular of infrared radiation. In this respect the utilization of pyroelectric crystals is highly promising.

Sec. 32. Direct Electric Current in Crystals

In the presence of an electric field $\boldsymbol{E}$ in conducting crystals an electric current of density $\boldsymbol{j}$ is generated. The fundamental equations for direct current in anisotropic media are the same as those for the isotropic media:

$$\operatorname{curl} \boldsymbol{E} = 0 \tag{32.1}$$

whence follows the existence of potential φ:

$$\boldsymbol{E} = -\operatorname{grad} \varphi, \tag{32.2}$$

and the equation of the continuity of current

$$\operatorname{div} \boldsymbol{j} = 0. \tag{32.3}$$

During the flow of electric current through a conducting material heat is liberated per unit volume per unit time

$$Q = \boldsymbol{E}\cdot\boldsymbol{j}. \tag{32.4}$$

In crystals Ohm's law is replaced by a general linear relation

$$\boldsymbol{j} = \boldsymbol{\sigma}\cdot\boldsymbol{E} \tag{32.5}$$

or

$$\boldsymbol{E} = \boldsymbol{\rho}\cdot\boldsymbol{j}, \tag{32.6}$$

where the second-rank tensor $\boldsymbol{\sigma}$ is called the *tensor of specific electrical conductivity*, and $\boldsymbol{\rho} = \boldsymbol{\sigma}^{-1}$ the *tensor of specific resistance*. With the

* Ferroelectrics constitute an important and peculiar group of pyroelectrics (see Sec. 65).

aid of these two tensors Joule's heat Q can be represented in two equivalent forms:

$$Q = \boldsymbol{E} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{E} = \sigma_{ik} E_i E_k, \tag{32.7}$$

$$Q = \boldsymbol{j} \cdot \boldsymbol{\rho} \cdot \boldsymbol{j} = \rho_{ik} j_i j_k. \tag{32.8}$$

Thermodynamics of irreversible processes permits essential improvement of formulas (32.5) and (32.6), i.e. making them more concrete. First, even though the symmetry of crystals of pyroelectric classes does not exclude the appearance in (32.5) and (32.6) of constant terms $\boldsymbol{j}^{(0)}$ and $\boldsymbol{E}^{(0)}$ respectively, the thermodynamics of irreversible processes states that these terms must be absent. Second, tensors $\boldsymbol{\sigma}$ and $\boldsymbol{\rho}$ must be symmetric. Third, all their eigenvalues must be positive (see Sec. 76).

The influence of the symmetry of crystals on their electrical conductivity is discussed in the same way as the influence of symmetry on their dielectric properties. Let us note that the eigenvectors of the tensors of dielectric properties and of the tensors characterizing electrical conductivity coincide only when their directions are determined by the symmetry elements of the crystal. The eigenvectors of tensors $\boldsymbol{\sigma}$ and $\boldsymbol{\rho}$ always coincide, since these tensors are mutually reciprocal.

Let us calculate the electrical conductivity of a crystal slab of area S and thickness d ($d \ll \sqrt{S}$); denote the unit vector of the normal to slab by $\boldsymbol{n}$. Insofar as the slab surfaces must be metallized, the field in the slab coincides with the field in a parallel-plate capacitor:

$$\boldsymbol{E} = (U/d)\, \boldsymbol{n}, \tag{32.9}$$

where U is the potential difference on the slab surfaces. Consequently, current density

$$\boldsymbol{j} = (U/d)\, \boldsymbol{\sigma} \cdot \boldsymbol{n}, \tag{32.10}$$

and the total current passing through the slab

$$I = S\boldsymbol{n} \cdot \boldsymbol{j} = (SU/d)\, \boldsymbol{n} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{n}. \tag{32.11}$$

Thus, in this case the normal component of the tensor of specific electrical conductivity plays the role of the specific electrical conductivity in the given direction. The resistance of the crystal slab is

$$\frac{U}{I} = \frac{d}{S} \frac{1}{\boldsymbol{n} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{n}}. \tag{32.12}$$

In a sense, quantity $1/(\boldsymbol{n} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{n})$ is the specific resistance of the crystal slab in direction $\boldsymbol{n}$; generally speaking, it is not equal to the normal component $\boldsymbol{n} \cdot \boldsymbol{\rho} \cdot \boldsymbol{n}$ of the tensor of specific resistance.

Let us discuss a problem which is, in a certain sense, an inverse of the preceding one: let us calculate the resistance of a crystal rod of length d and cross-section area S ($d \gg \sqrt{S}$); the unit vector $\boldsymbol{n}$ de-

termines the direction of the rod axis. Obviously, in this case

$$\boldsymbol{j} = (I/S)\,\boldsymbol{n}, \tag{32.13}$$

whence

$$\boldsymbol{E} = (I/S)\,\boldsymbol{\rho}\cdot\boldsymbol{n}, \tag{32.14}$$

and the potential difference at the ends of the rod

$$U = d\boldsymbol{n}\cdot\boldsymbol{E} = (Id/S)\,\boldsymbol{n}\cdot\boldsymbol{\rho}\cdot\boldsymbol{n}. \tag{32.15}$$

Under these conditions the role of specific resistance in direction $\boldsymbol{n}$ is played by the normal component of the specific resistance tensor $\boldsymbol{n}\cdot\boldsymbol{\rho}\cdot\boldsymbol{n}$, while the role of specific electrical conductivity by a converse quantity $1/(\boldsymbol{n}\cdot\boldsymbol{\rho}\cdot\boldsymbol{n})$.

It can be concluded from these two problems that such expressions as "the magnitude of specific resistance in a given direction", "the magnitude of specific electrical conductivity in a given direction" and generally "the quantity characterizing a property in a given direction" acquire definite meaning only when the conditions, in which the given property is measured, are known (compare (30.8) and (30.12)).

Sec. 33. Thermal Conductivity of Crystals

Thermal conductivity of isotropic solids is determined from the proportionality of the heat flow $\boldsymbol{q}$ and temperature gradient grad T:

$$\boldsymbol{q} = -\lambda \operatorname{grad} T \tag{33.1}$$

(the minus sign was chosen so that the thermal conductivity coefficient λ is always regarded positive: heat flows in the direction of temperature decrease. A natural generalization of this regularity for anisotropic solids is

$$\boldsymbol{q} = -\boldsymbol{\lambda}\cdot\operatorname{grad} T. \tag{33.2}$$

This formula is fully similar to the formula of the theory of electrical conductivity of crystals (32.4) which can be written

$$\boldsymbol{j} = -\boldsymbol{\sigma} \operatorname{grad} \varphi. \tag{33.3}$$

The tensor of thermal conductivity $\boldsymbol{\lambda}$, just as the tensor of electrical conductivity $\boldsymbol{\sigma}$, is symmetric and all its eigenvalues are positive.

Evidently, div $\boldsymbol{q}$ is equal to the quantity of heat liberated by a unit volume of a solid per unit time. The change of temperature in this volume per unit time is equal to —div $\boldsymbol{q}$ divided by the heat capacity of unit volume, i.e. by $c\rho$ where c is the specific heat capacity (heat capacity of unit of mass) and ρ is the density of the solid. Hence, the equation of the thermal conductivity of crystals is

$$\frac{\partial T}{\partial t} = -\frac{1}{c\rho}\operatorname{div}\boldsymbol{q} = \frac{1}{c\rho}\operatorname{div}(\boldsymbol{\lambda}\cdot\operatorname{grad} T). \tag{33.4}$$

Insofar as the thermal conductivity tensor λ, as well as ρ and c, does not depend on the coordinates, it can be removed beyond the sign of differentiation and a *tensor of thermal diffusivity* $\boldsymbol{k} = (1/\rho c)\,\lambda$ can be introduced, thereupon writing the equation of thermal conductivity thus:

$$\frac{\partial T}{\partial t} = k_{ij}\frac{\partial^2 T}{\partial x_i\,\partial x_j}. \tag{33.5}$$

If in each point of a body $\partial T/\partial t = 0$, then we have to deal with a steady heat flow not varying with time. In this case, neglecting factor $1/c\rho$ which is now irrelevant, we obtain from (33.5) the equation

$$\lambda_{ij}\frac{\partial^2 T}{\partial x_i\,\partial x_j} = 0, \tag{33.6}$$

which is fully similar to the equation for the potential in the theory of direct current. Under these conditions the thermal conductivity of crystal rods and slabs is evidently calculated with the aid of formulas fully similar to those obtained in the preceding section. To the potential difference here corresponds the temperature difference, to the current intensity—the quantity of heat passing through a rod or plate per 1 C/s, to the electric field intensity—the temperature gradient with a reverse sign, to the vector of current density, the vector of heat flow.

Let us discuss temperature fields produced in crystals under uniform heating, i.e. by the increase of ambient temperature at a constant rate of h [C/s]. Naturally, uniform cooling is discussed in the same way, only h has a negative value in this case. After a certain time of ajustment* it can be assumed with a sufficient degree of accuracy that the temperature at each point of the crystal rises at a rate of h. Then the solution of the thermal conductivity equation (33.5) can be found in the form

$$T(\boldsymbol{r},\ t) = \Phi(\boldsymbol{r}) + ht; \tag{33.7}$$

function Φ satisfies the equation

$$k_{ij}\frac{\partial^2 \Phi}{\partial x_i\,\partial x_j} = h. \tag{33.8}$$

Let a crystal plate, $2a$ thick, be uniformly heated from the surfaces $\boldsymbol{n}\cdot\boldsymbol{r} = \pm a$. Here $\boldsymbol{n}$ is the unit vector of a perpendicular to the plane of the plate, $\boldsymbol{r}$ is the radius-vector taken from some point in the middle plane of the plate. Let us introduce coordinate $z =$

* Its duration is proportional to the square of the body linear dimensions, inversely proportional to the thermal diffusivity and depends on the heat exchange conditions at the boundary of the body, essentially increasing with their deterioration.

$= \boldsymbol{n} \cdot \boldsymbol{r} = n_i x_i$. Obviously, temperature is a function of z and time t. Noticing that

$$\frac{\partial}{\partial x_i} = \frac{\partial z}{\partial x_i} \frac{\partial}{\partial z} = n_i \frac{\partial}{\partial z}$$

equation (33.8) will now be

$$k_{ij} n_i n_j \frac{d^2 \Phi}{dz^2} = h, \tag{33.9}$$

and, since ambient temperature on both sides of the plate is the same, $\Phi(-a) = \Phi(a)$. Therefore, the solution of (33.9) is

$$\Phi(z) = \frac{h}{2k_{ij} n_i n_j} z^2 + B, \tag{33.10}$$

where B is a constant, yet unknown, determined from the boundary conditions. If in particular, it is assumed that temperature $T(\pm a, t)$ at the boundary of the crystal is equal to ambient temperature $T_0(t)$, then

$$B = T_0(0) - \frac{ha^2}{2k_{ij} n_i n_j}.$$

Crystals are usually heated in air or in some other gas, the temperature of the surface crystal layers being to a greater or lesser degree lower than the ambient temperature. The boundary condition corresponding to this case, if no account is taken of the heat exchange due to irradiation, has the form

$$\frac{\partial T(\pm a, t)}{\partial z} = \pm H [T_0(t) - T(\pm a, t)], \tag{33.11}$$

where the coefficient H characterizes the heat exchange conditions at the interface between the crystal and its environment: $H = 0$ corresponds to a complete absence of heat flow across the crystal surface, at $H \to \infty$ the temperature of the crystal surface layers $T(\pm a, t)$ tends to reach the level of ambient temperature $T_0(t)$. Under boundary condition (33.11)

$$B = T_0(0) - \frac{ha^2}{2k_{ij} n_i n_j} - \frac{ha}{H k_{ij} n_i n_j};$$

apparently, exactly the last term characterizes the temperature lag of the crystal surface layers.

It is difficult to determine coefficient H; in particular, its dependence on the direction of the normal to the face of the crystal bordering on its environment has not been experimentally investigated yet. However, some important data on the distribution of temperature within the crystal can be obtained without knowing this coefficient. As will be shown in Sec. 55, it will suffice to know the difference between the temperature of the crystal at a given point $T(z, t)$

and its average temperature $\langle T(t)\rangle$ for calculating the stresses developing in the crystal at its heating (or cooling). In this case

$$\langle T(t)\rangle = \frac{1}{2a}\int_{-a}^{a} T(z, t)\,dz.$$

In calculating the difference $T - \langle T\rangle$, term B as well as term ht drops out, and for the case of uniform heating of a crystal at a rate of h, we obtain

$$T - \langle T\rangle = \frac{ha^2}{2k_{ij}n_i n_j}\left[\left(\frac{z}{a}\right)^2 - \frac{1}{3}\right]. \qquad (33.12)$$

On the symmetry of the physical properties of crystals see P. Curie (1909); Wigner (1971), as well as textbooks on crystal physics: Voigt (1928); Wooster (1949, 1958, 1977); Shubnikov, Flint and Bokyi (1940); Nye (1957); Koptsik (1958); Bhagavantam (1966); Mason (1966); Kleber, Meyer, Schoenborn (1968); Vasiliev (1972); Perelomova and Tagieva (1972); Sonin (1976); Shaskolskaya (1976, 1978a); Donnay (1973); Hartmann (1973).

On electrical properties and thermal conductivity of crystals see Ioffe (1932); Born, Huang (1958); Landau and Lifshits (1957 and 1965); Zhdanov (1961); Kittel (1975); Zheludev (1968, 1969, 1976); Slater (1969).

Chapter IV

OPTICAL PROPERTIES OF CRYSTALS

Sec. 34. Electromagnetic Waves in Transparent Crystals

The propagation of electromagnetic waves in a **transparent non-magnetic** crystal is defined by Maxwell's equations

$$\operatorname{curl} \boldsymbol{H} = \frac{1}{c}\frac{\partial \boldsymbol{D}}{\partial t}, \quad \operatorname{curl} \boldsymbol{E} = -\frac{1}{c}\frac{\partial \boldsymbol{H}}{\partial t}, \tag{34.1}$$

$$\operatorname{div} \boldsymbol{D} = 0, \quad \operatorname{div} \boldsymbol{H} = 0 \tag{34.2}$$

and the material equation

$$\boldsymbol{E} = \boldsymbol{\eta}\cdot\boldsymbol{D}, \quad E_i = \eta_{ik} D_k. \tag{34.3}$$

Here $\boldsymbol{E}$ and $\boldsymbol{H}$ are vectors of the electric and magnetic field intensity respectively, $\boldsymbol{D}$ is the vector of electric induction, c is the velocity of light. There are no terms corresponding to the electric current and free charges, since it is assumed that the crystal is transparent and thus is an ideal dielectric. If the crystal is non-magnetic, the vectors of the magnetic field intensity $\boldsymbol{H}$ and magnetic induction $\boldsymbol{B}$ are equal to each other.

The dielectric impermeability tensor $\boldsymbol{\eta}$ depends on frequency; at optical frequencies ($\omega \sim (2.5\text{-}5)\cdot 10^{15}\,\mathrm{s}^{-1}$), i.e. in the visible, ultraviolet and infrared regions of the spectrum, its eigenvalues are much closer to unity than in static or slowly varying fields. For the majority of crystals the eigenvalues of $\boldsymbol{\eta}$ (in the visible part of the spectrum) range from 0.17 for diamonds to 0.62 for ice. Tensor $\boldsymbol{\eta}$ is symmetric, as in electrostatics: the proof of this is based on the thermodynamics of irreversible processes*.

If a variable electromagnetic field travels through a crystal as a plane electromagnetic wave, the dependence of field vectors $\boldsymbol{E}$, $\boldsymbol{D}$, $\boldsymbol{H}$ on spatial coordinates $\boldsymbol{r}$ and time t is defined by equations

$$\begin{aligned} \boldsymbol{E}(\boldsymbol{r}, t) &= \boldsymbol{E}_0 \exp(i\boldsymbol{k}\cdot\boldsymbol{r} - i\omega t), \\ \boldsymbol{D}(\boldsymbol{r}, t) &= \boldsymbol{D}_0 \exp(i\boldsymbol{k}\cdot\boldsymbol{r} - i\omega t), \\ \boldsymbol{H}(\boldsymbol{r}, t) &= \boldsymbol{H}_0 \exp(i\boldsymbol{k}\cdot\boldsymbol{r} - i\omega t), \end{aligned} \tag{34.4}$$

---

* See Landau and Lifshits (1957, Secs. 76, 88). The symmetry of the permittivity tensor is proved there. Evidently, its reverse—the impermeability tensor—is also symmetric.

Here ω is the cyclic frequency, $\boldsymbol{k}$ is the wave vector; it is normal to the plane of the wave front and is connected with other wave characteristics by relations

$$\boldsymbol{k} = \frac{2\pi}{\lambda}\boldsymbol{m} = \frac{\omega}{v}\boldsymbol{m} = \frac{\omega}{c}n\boldsymbol{m}, \tag{34.5}$$

in which $\boldsymbol{m}$ is the unit vector of the wave normal, λ is the wavelength, v is its phase velocity in the given medium. The ratio between the velocity of the electromagnetic wave in vacuum and its phase velocity in the given medium

$$n = c/v \tag{34.6}$$

is called the *refractive index* of this electromagnetic wave in the medium. The same definition of the refractive index is used for the wave in an anisotropic medium.

As has already been noted, when generalizing the characteristics of a substance used in the physics of isotropic media for anisotropic media, it is necessary to point out the exact method of generalization. This has been done in the above definition: in the optics of isotropic media the refractive index n for a given medium is, on the one hand

$$n = \frac{\sin i}{\sin r},$$

where i is the angle of incidence, r is the angle of refraction, and, on the other hand, it is equal to the ratio of the phase velocities of light in vacuum and in the medium (34.6). It is this second property of the refractive index that is used in the generalization of the concept for the anisotropic medium.

In an electromagnetic wave travelling through an anisotropic medium the spatial relations between field vectors $\boldsymbol{D}$, $\boldsymbol{H}$, and $\boldsymbol{E}$ are much more complicated than in the case of an isotropic medium. They are defined by Maxwell's equations (34.1) and (34.2); expressions (34.4) for the field vectors of the wave must be substituted into these expressions. The effect of the operations curl, div and d/dt on the exponential vector functions of type (34.4) comes to the vector and scalar multiplication by $i\boldsymbol{k}$ and $-i\omega$ respectively. Therefore, equations (34.1) for plane waves take the form

$$\boldsymbol{k} \times \boldsymbol{H} = -\frac{\omega}{c}\boldsymbol{D}, \quad \boldsymbol{k} \times \boldsymbol{E} = \frac{\omega}{c}\boldsymbol{H}, \tag{34.7}$$

and Eqs. (34.2) become

$$\boldsymbol{k}\cdot\boldsymbol{D} = 0, \quad \boldsymbol{k}\cdot\boldsymbol{H} = 0. \tag{34.8}$$

Equations (34.8) mean only the perpendicularity of vectors $\boldsymbol{D}$ and $\mathbf{H}$ to the wave vector $\boldsymbol{k}$; since this already follows from (34.7), equations (34.8) can be simply omitted. Vectors $\boldsymbol{D}$ and $\boldsymbol{H}$ lie in the plane of the wave front, this being the effect of the transversal char-

acter of electromagnetic waves in anisotropic media. Moreover, it follows from (34.7) that vectors $\boldsymbol{H}$ and $\boldsymbol{D}$ as well as vectors $\boldsymbol{H}$ and $\boldsymbol{E}$ are mutually perpendicular (Fig. 34.1).

Thus, in an anisotropic medium there remain the orthogonality and phase coincidence of vectors $\boldsymbol{E}$ and $\boldsymbol{H}$ as well as of vectors $\boldsymbol{D}$ and $\boldsymbol{H}$, but the collinearity of vectors $\boldsymbol{D}$ and $\boldsymbol{E}$ disappears.

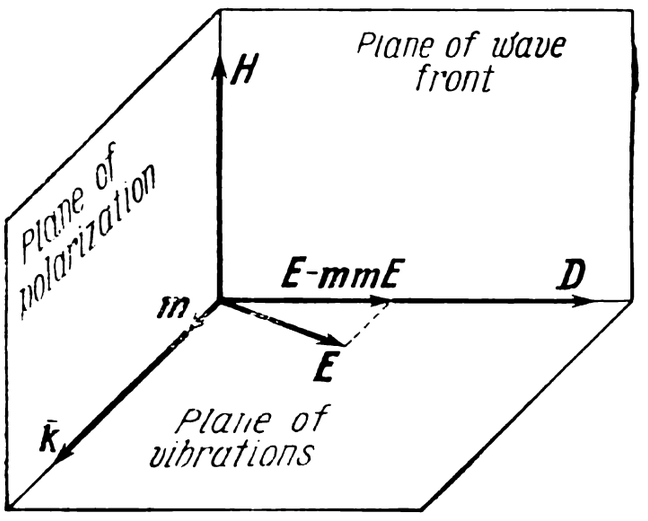


Fig. 34.1. Space relations between field vectors of an electromagnetic wave in a non-magnetic anisotropic medium

Cancelling out ω/c in equation (34.7) we write Maxwell's equations for plane electromagnetic waves in an anisotropic medium as

$$\boldsymbol{nm} \times \boldsymbol{H} = -\boldsymbol{D}, \quad \boldsymbol{nm} \times \boldsymbol{E} = \boldsymbol{H}. \tag{34.9}$$

Eliminating from them the magnetic field intensity $\boldsymbol{H}$, we obtain the relation between the electric field vector and the electric induction vector in a plane electromagnetic wave

$$n^2\boldsymbol{m} \times (\boldsymbol{m} \times \boldsymbol{E}) = -\boldsymbol{D},$$

which upon elementary transformations appears as

$$\boldsymbol{E} - \boldsymbol{mm} \cdot \boldsymbol{E} = \frac{1}{n^2}\boldsymbol{D}. \tag{34.10}$$

The left-hand side of (34.10) is the component of vector $\boldsymbol{E}$ lying in the plane of the wave front (Fig. 34.1). It is collinear with the electric induction vector, while the ratio of its length to the length of the induction vector $\boldsymbol{D}$ is equal to the square of the ratio between the wave velocity in the medium and its velocity in vacuum. The electromagnetic wave is still transversal, but only induction vectors lie in the plane of the wave front, while the intensity vectors $\boldsymbol{E}$ can leave this plane.

With the aid of material equation (34.3) we shall also eliminate $\boldsymbol{E}$ from relation (34.10):

$$(\eta - \boldsymbol{mm}\cdot\eta)\cdot\boldsymbol{D} = \frac{1}{n^2}\boldsymbol{D}, \quad (\eta_{ik} - m_i m_j \eta_{ik}) D_k = \frac{1}{n^2} D_i. \qquad (34.11)$$

The obtained vector equation determines the velocity and polarization of the electromagnetic wave travelling across the crystal in the direction $\boldsymbol{m}$ of the wave. For its investigation we introduce a special Cartesian system of coordinates X_1, X_2, X_3; the axis X_3 is directed along the normal to the wave ($\boldsymbol{e}_3 = \boldsymbol{m}$) and the mutually perpendicular axes X_1 and X_2 will be in the plane of the wave front. In this special system $D_3 = 0$ because of the transversal character of the electric induction vector, and for this system we rewrite vector equation (34.11)

$$\begin{aligned} \eta_{11}D_1 + \eta_{12}D_2 &= n^{-2}D_1, \\ \eta_{12}D_1 + \eta_{22}D_2 &= n^{-2}D_2; \end{aligned} \qquad (34.12)$$

this being reduced to two scalar equations only, the third one being a trivial identity $0 = 0$.

The system of equations (34.12) shows that n^{-2} is the eigenvalue of the two-dimensional symmetric tensor with the components

$$\begin{Vmatrix} \eta_{11} & \eta_{12} \\ \eta_{12} & \eta_{22} \end{Vmatrix},$$

and $\boldsymbol{D}$ is its eigenvector. This tensor can be naturally called the projection of the dielectric impermeability tensor onto the plane of the wave front. Since it is two-dimensional, it has only two eigenvalues—the roots of a quadratic equation

$$\begin{vmatrix} \eta_{11} - n^{-2} & \eta_{12} \\ \eta_{12} & \eta_{22} - n^{-2} \end{vmatrix} = 0; \qquad (34.13)$$

apparently they are equal to

$$n_{(1,2)}^{-2} = \frac{1}{2}\left[(\eta_{11} + \eta_{22}) \pm \sqrt{(\eta_{11} - \eta_{22})^2 + (2\eta_{12})^2}\right]. \qquad (34.14)$$

Thus the velocity of electromagnetic waves travelling across the crystal in the direction $\boldsymbol{m}$ is either $v_{(1)} = c/n_{(1)}$ or $v_{(2)} = c/n_{(2)}$.

To each eigenvalue $n_{(q)}^{-2}$ there corresponds an eigenvector $\boldsymbol{D}^{(q)}$. The direction of the electric induction vector in a wave travelling with a velocity $v_{(1)}$ is defined by any of the two equivalent equations

$$\begin{aligned} (\eta_{11} - n_{(1)}^{-2})\, D_1^{(1)} + \eta_{12}D_2^{(1)} &= 0, \\ \eta_{12}D_1^{(1)} + (\eta_{22} - n_{(1)}^{-2})\, D_2^{(1)} &= 0; \end{aligned} \qquad (34.15)$$

the direction of vector $\boldsymbol{D}^{(2)}$ can be found similarly, but it is simpler to utilize the mutual perpendicularity of vectors $\boldsymbol{D}^{(1)}$ and $\boldsymbol{D}^{(2)}$ (the

eigenvectors corresponding to non-coincident eigenvalues are mutually orthogonal, see Sec. 19).

Let, in particular, the coordinate axes X_1 and X_2 in the wave front plane be chosen so that $\eta_{12} = 0$ and $\eta_{11} > \eta_{22}$. Then the refractive indices are $n_{(1)} = 1/\sqrt{\eta_{11}}$, $n_{(2)} = 1/\sqrt{\eta_{22}}$ and the induction vectors $\boldsymbol{D}^{(1)} \parallel X_1$, $\boldsymbol{D}^{(2)} \parallel X_2$.

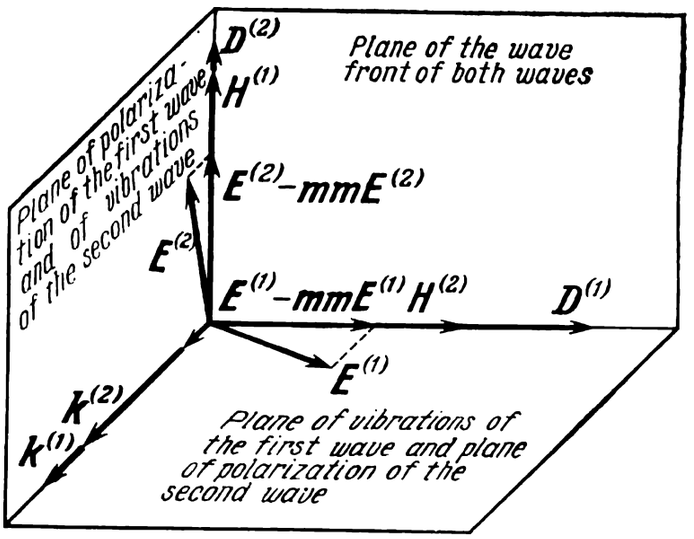


Fig. 34.2. Polarization and vibration planes of two waves in case of birefringence

So, a double refraction of light occurs in crystals: monochromatic light passing through a crystal in a specified direction $\boldsymbol{m}$ splits generally into two linear-polarized waves that propagate with different velocities $v_{(1)}$ and $v_{(2)}$. The polarization planes of these two waves are mutually perpendicular (Fig. 34.2).

Sec. 35. Optical Indicatrix

Calculations performed in Sec. 34 can be illustrated by a simple geometric construction. The indicatrix of the dielectric impermeability tensor $\boldsymbol{\eta}$

$$\boldsymbol{r}\cdot\boldsymbol{\eta}\cdot\boldsymbol{r} = 1, \quad \eta_{ik}x_i x_k = 1 \tag{35.1}$$

is an ellipsoid with its centre at the origin of the coordinates and is called an *optical indicatrix* of the crystal (it can be proved that all the eigenvalues of tensor $\boldsymbol{\eta}$ are positive (see Sec. 22)).

Let us consider the central section of an optical indicatrix by a plane of the wave front: it is an ellipse, all points of which satisfy both the indicatrix equation (35.1) and the equation of the plane of the wave front passing through the origin, $x_3 = 0$. The equation

of this ellipse (in the same special system of coordinates) is

$$\eta_{11}x_1^2 + 2\eta_{12}x_1x_2 + \eta_{22}x_2^2 = 1. \tag{35.2}$$

If axes X_1 and X_2 of the special system of coordinates are directed along the eigenvectors of a two-dimensional tensor

$$\begin{Vmatrix} \eta_{11} & \eta_{12} \\ \eta_{12} & \eta_{22} \end{Vmatrix},$$

then, since the eigenvalues of the tensor are $n_{(1)}^{-2}$ and $n_{(2)}^{-2}$, the equation of the ellipse will be

$$\left(\frac{x_1}{n_{(1)}}\right)^2 + \left(\frac{x_2}{n_{(2)}}\right)^2 = 1. \tag{35.3}$$

Hence it is clear that $n_{(1)}$ and $n_{(2)}$ are the lengths of the principal semi-axes of the ellipse. The electric induction vectors $\boldsymbol{D}^{(1)}$ and $\boldsymbol{D}^{(2)}$ will also be directed along these sem-axes.

Thus, to find the velocities and polarizations of the electromagnetic waves travelling across a crystal in any given direction, it will suffice to consider the central section of the optical indicatrix by the plane of the wave front, i.e. by the plane perpendicular to the ray direction. The directions of the principal semi-axes of this section coincide with the directions of the electric induction vectors of the given wave, and the lengths of these principal semi-axes are equal to their refractive indices.

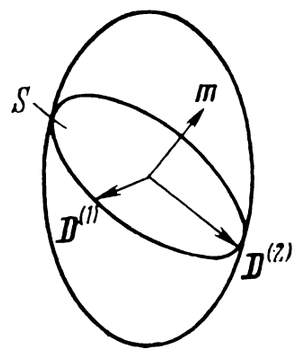


Fig. 35.1. Central section of the optical indicatrix of a uniaxial crystal by the wave front plane

The scheme of the optical indicatrix is shown in Fig. 35.1. S is the central section perpendicular to the direction of the wave propagation, $\boldsymbol{m}$ is the vector of the wave normal. The semi-axes of the ellipse are equal in magnitude to $n_{(1)}$ and $n_{(2)}$. For waves with the refractive index $n_{(1)}$ the plane of the vector $\boldsymbol{D}^{(1)}$ vibrations passes through $\boldsymbol{D}^{(1)}$ and $\boldsymbol{m}$, for a wave with index $n_{(2)}$, through $\boldsymbol{D}^{(2)}$ and $\boldsymbol{m}$.

So, it is necessary to know the magnitude of the semi-axes of the optical indicatrix, its form and its orientation in the crystal in order to determine the velocity, refractive indices and vibration planes for waves propagating in the crystal in any direction.

The absolute values of the optical indicatrix semi-axes N_1, N_2, N_3* are the characteristic parameters of a given substance. It must be remembered that they depend on the frequency of the electro-

* n denotes refractive indices in an arbitrary direction, N is for the refractive indices in the direction of the principal axes, i.e. for the principal refractive indices.

magnetic field vibrations*. As to the form and orientation of the indicatrix, they are fully determined by the crystal symmetry (see Sec. 22):

Category of crystal	Values of N	Form of the optical indicatrix	Optical properties of crystal
Higher	$N_1 = N_2 = N_3$	Sphere	Isotropic
Intermediate	$N_1 = N_2 \neq N_3$	Ellipsoid of revolution	Uniaxial
Lower	$N_1 \neq N_2 \neq N_3$	Triaxial ellipsoid	Biaxial

In crystals of the higher category the optical indicatrix is a sphere of radius $N = 1/\sqrt{\eta}$. All its central sections are circular, all refractive indices are equal to each other, and there is no birefringence. In respect of their optical properties crystals of the higher category are isotropic.

In crystals of the intermediate and lower categories a monochromatic light generally breaks up into two plane-polarized waves. However, in all these crystals there are singular directions—*optic axes* or *binormals* whose characteristic feature is that a section of the optical indicatrix by the wave front plane perpendicular to them is a circumference. At any choice of the X_1 and X_2 axes in the wave front plane, perpendicular to the optic axis, the projection of the dielectric impermeability tensor onto this plane will have components $\begin{Vmatrix} \eta_{11} & 0 \\ 0 & \eta_{11} \end{Vmatrix}$, so that both roots of (34.13) will coincide: $n_{(1)}^{-2} = n_{(2)}^{-2} = \eta_{11}$. Any vector in the plane of the wave front serves as the eigenvector of this two-dimensional tensor. Therefore, light of any polarization can travel along the optic axis.

In isotropic bodies and in the cubic system crystals where the optical indicatrix is a sphere and all its central sections are circular, any direction can be regarded as an optic axis.

In crystals of the intermediate category the optical indicatrix is an ellipsoid of revolution, with equation (in the crystal-physical system of coordinates)

$$\frac{x_1^2 + x_2^2}{N_o^2} + \frac{x_3^2}{N_e^2} = 1. \tag{35.4}$$

The axis of rotation of the ellipsoid coincides with the principal symmetry axis of the crystal and is its only optic axis, while its only circular section perpendicular to the principal symmetry axis of the crystal has radius N_0. The crystals of the intermediate cate-

* As well as on the influence of external factors, such as temperature, electric field, mechanical stress, etc. (see Ch. IX).

gory are optically uniaxial. The binormal of the optical indicatrix coincides with the principal symmetry axis of the crystal.

In crystals of the lower category the optical indicatrix is a triaxial ellipsoid; in the system of coordinates constructed on the eigenvectors of the dielectric tensors for a given frequency* its equation is

$$\left(\frac{x_1}{N_1}\right)^2+\left(\frac{x_2}{N_2}\right)^2+\left(\frac{x_3}{N_3}\right)^2=1. \qquad (35.5)$$

Here N_1, N_2, N_3 are the principal refractive indices: their inverse squares are equal to the eigenvalues of the dielectric impermeability tensor. These indicatrices have two circular sections and correspondingly two binormals, i.e. two optic axes P_1 and P_2 (Fig. 35.2),

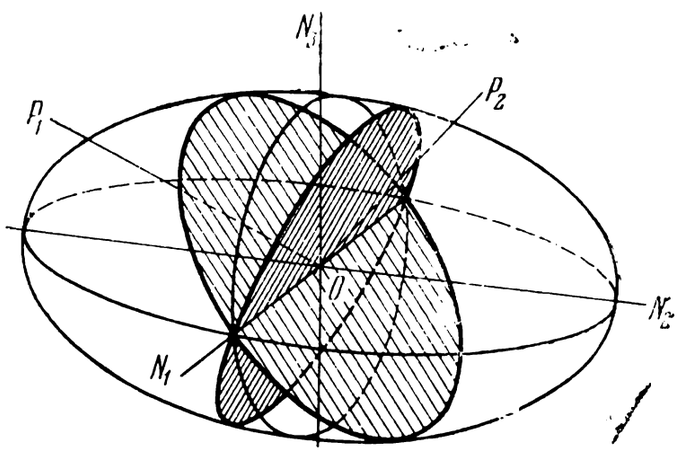


Fig. 35.2. Central sections of the optical indicatrix of a biaxial crystal

the lower category crystals being thus optically biaxial. Equation (35.1) and its geometric interpretation in the form of an optical indicatrix permit a lucid description of the optical properties of crystals.

In crystals of the intermediate category the orientation of the optic axis is fully defined by the crystal symmetry: the optic axis (binormal) is always the [001] or [0001] direction, i.e. the principal axis of the crystal symmetry; the basal plane (001) or (0001) is the optically isotropic section.

It follows from (35.4) that in optically uniaxial crystals one of the refractive indices, $n_{(1)}$, does not depend on the direction, and the other one, $n_{(2)}$, is different in different directions. The first one is usually called "ordinary" and is denoted by n_o (or N_o). The second index is called "extraordinary" and is denoted by n_e. Its values, depending on the direction of wave propagation, vary from N_o to the extreme value N_e. Thus, $n_o = N_o$, while n_e varies from N_o to N_e.

The descriptions "ordinary" and "extraordinary" are due to the

* This system coincides with the crystal-physical one only for rhombic crystals, in monoclinic crystals it has an axis common with the crystal-physical system.

fact that in a wave with refractive index n_o the ray coincides with the wave normal, as in ordinary waves in an isotropic medium, while in a wave with refractive index n_e the ray diverges from the wave normal (see Sec. 36).

The birefringence of a crystal is measured by the difference $\Delta N = N_e - N_o$. If $(N_e - N_o) > 0$, uniaxial crystals are regarded as optically positive; the optical indicatrix is an ellipsoid of revolution prolate along the optic axis. If $(N_e - N_o) < 0$, the indicatrix is an oblate ellipsoid of revolution, crystals are optically negative (Fig. 35.3). Quartz is an example of uniaxial positive crystals, calcite (Iceland spar), potassium or ammonium dihydrophosphate

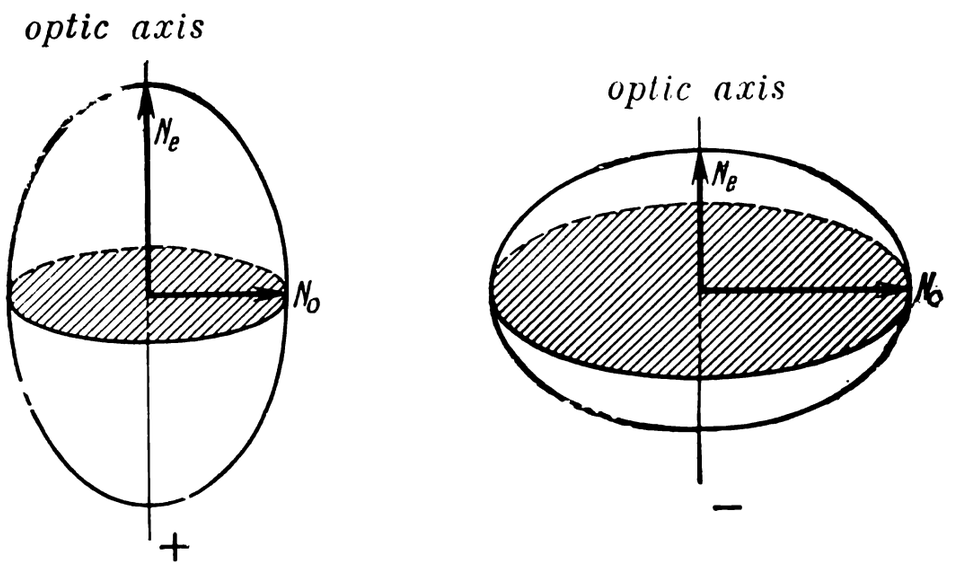


Fig. 35.3. Optical indicatrices of positive and negative optically uniaxial crystals

(KDP or ADP) are examples of uniaxial negative crystals. Oblateness or prolateness of ellipsoids in Fig. 35.3 is greatly exaggerated. Only in such strongly birefringent crystals as calcite, saltpetre, rutile the difference between N_e and N_o reaches 10%. Selenium and tellurium have enormous birefringence in the infrared region of the spectrum. For the majority of crystals, however, the difference between N_e and N_o does not exceed fractions of one per cent.

In crystals of the lower category both refractive indices are "extraordinary", i.e. their magnitude depends on the direction, and the incident and refracted beams do not lie in the same plane. The crystals are optically biaxial. Their optical indicatrix is a triaxial ellipsoid and has two circular sections. The line of intersection of the circular sections is the middle principal axis of the optical indicatrix; it is perpendicular to the plane of the optic axes. The major and minor principal axes of the optical indicatrix are the bisectrices of the angles between optic axes. The optical indicatrix symmetry is *mmm*.

In crystals of the rhombic system the principal axes of the optical indicatrix coincide with the crystallographic axes, i.e. with 2-fold axes or with perpendicular to plane m, and the plane of optic axes coincides with planes (100), (001) or (010).

In monoclinic crystals one of the indicatrix axes always passes along a 2-fold symmetry axis or along a perpendicular to m, i.e. coincides with axis X_2, while the directions of two other axes situated in the (010) plane do not depend on crystal symmetry. The

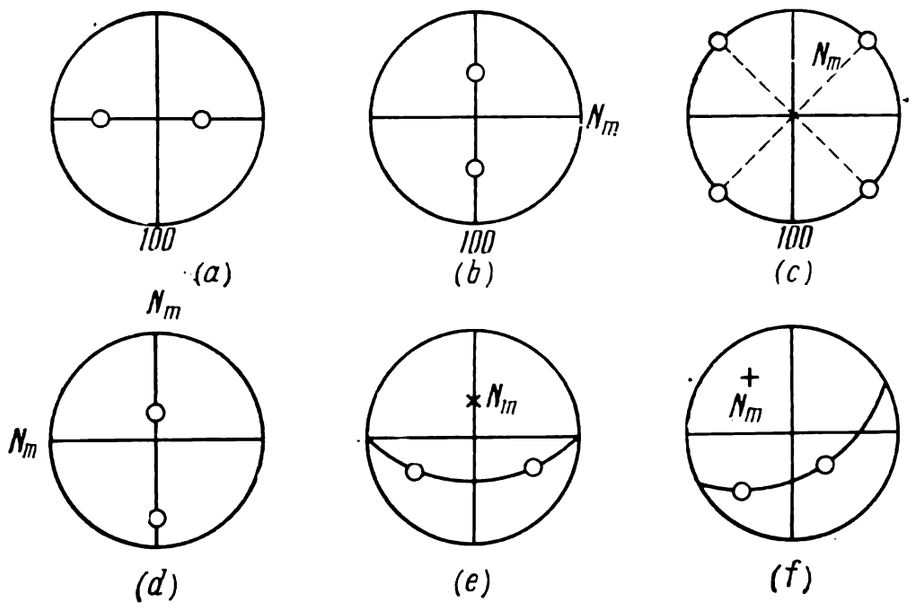


Fig. 35.4. Stereographic projections of the indicatrix axes and of optic axes planes in biaxial crystals: rhombic crystals (a, b, c), monoclinic crystals (d, e) and triclinic crystals (f)

plane of optic axes is either parallel to the only symmetry plane or is in the plane of the zone to which the X_2 axis belongs.

Finally, in triclinic crystals the orientation of the optical indicatrix generally is in no way connected with crystal symmetry and has to be determined for each substance individually.

The stereographic projections of the optic axes and of the principal axes of the indicatrix in crystals of the lower category are shown in Fig. 35.4.

For denoting the principal refractive indices corresponding to the semi-axes of the optical indicatrix of a crystal, standard notation is sometimes used: N_g, for the highest refractive index, N_m, for the mean refractive index, N_p for the lower one. In such a notation for a uniaxial crystal the magnitude of birefringence $\Delta N = N_g - N_p$, and for a biaxial crystal $N_g - N_m$, $N_g - N_p$, $N_m - N_p$, but usually the biaxial crystals are characterized only by the maximum difference $\Delta N = N_g - N_p$. It should be noted that the

magnitude of birefringence and the refractive indices are measured by different methods and to different degrees of accuracy.

Angle V between the major principal axis of the optical indicatrix of a biaxial crystal and the optic axis is determined by the formula

$$\tan V = \sqrt{\frac{N_p^{-2} - N_m^{-2}}{N_m^{-2} - N_g^{-2}}}, \tag{35.6}$$

while the angle between optical axes is $2V$. A biaxial crystal is called *optically positive*, if $2V < 90°$ and the major principal axis of the indicatrix is the bisectrix of the acute angle and the minor axis, of the obtuse angle; a biaxial crystal is *optically negative* if $2V > 90°$, the major principal axis of the indicatrix is the bisectrix of the obtuse angle and the minor axis, of the acute angle. If the mean refractive index N_m is close to the largest N_g or to the smallest N_p then angle V will be close to 0 or 90°, and the crystal will be close in its optical properties to the positive or negative uniaxial crystals respectively. If, on the contrary, the mean refractive index N_m satisfies the equality

$$2N_m^{-2} = N_p^{-2} + N_g^{-2}$$

then the optic axes are mutually perpendicular ($V = 45°$), the crystal is neither positive, nor negative and in its optical properties it is very far from being uniaxial.

It should be noted that all these definitions make sense for a given length of the light wave and at a definite temperature. Cases are possible, because of the dispersion of light, when one and the same substance will optically be positive for one wavelength and negative for another (see Sec. 39).

So, to obtain full characteristics of the optical properties of crystals it is necessary to measure the following quantities:

For crystals of the higher category — N.

For crystals of the intermediate category — N_g, N_p, optical sign.

For crystals of the lower category — N_g, N_m, N_p.

Besides, for crystals of the lower category it is necessary to determine the orientation of the principal axes of the optical indicatrix and the directions of the binormals.

In conclusion let us emphasize once more the great difference between the character of the propagation of electromagnetic waves in isotropic and anisotropic media. In an isotropic transparent medium light waves of any polarization can propagate in every direction; the same can be said of the mixture of light waves of all possible polarizations, i.e. of natural light. On the contrary, in an anisotropic transparent medium there can propagate in a given direction (if it is not an optic axis) light waves of only two strictly definite polarizations, and for that matter with different velocities, while natural

light (i.e. light of arbitrary polarization) can propagate only along optic axes.

As will be shown later, the differences in the symmetry of crystals lead to the differences in the character of polarization of the light propagating in the crystals: linear polarization is characteristic of the centrosymmetrical crystals, elliptic and circular polarizations, of the non-centrosymmetrical crystals.

This character of light propagation in crystals is connected neither with any peculiar properties of electromagnetic waves, nor with the internal structure of crystals, but solely with their anisotropy. Elastic waves propagating in an anisotropic medium are also polarized in a strictly definite manner (see Sec. 56).

Sec. 36. Waves and Rays. Principle of Duality. Fresnel's Ellipsoid

The vector of energy flow (the Poynting vector) in an electromagnetic wave is known to be

$$S=\frac{c}{4\pi}E\times H; \tag{36.1}$$

a unit vector s of this direction is called a *ray vector*. If an opaque screen with a sufficiently narrow diaphragm* is placed in the path

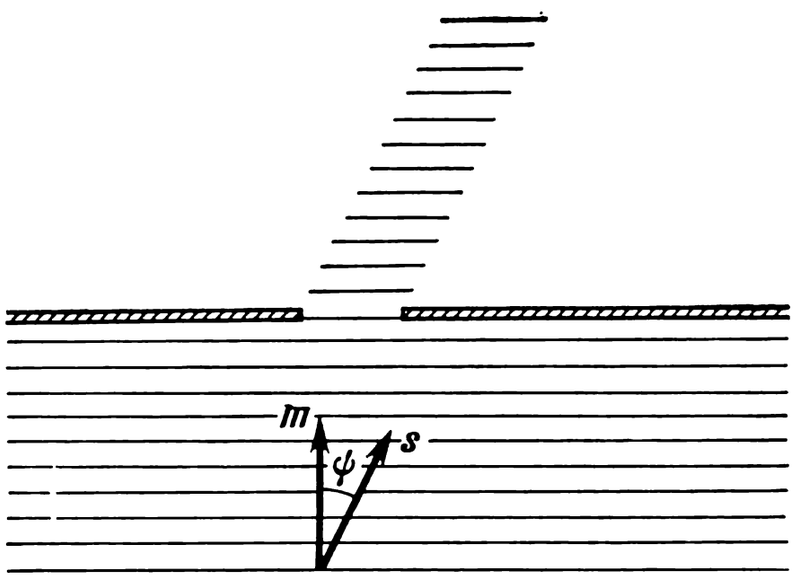


Fig. 36.1. Wave and ray in an anisotropic medium

of a light wave through a transparent crystal, the direction of a ray that passed through the diaphragm is determined by this particular vector s (Fig. 36.1).

* The width of the diaphragm must be, however, much larger than the light wavelength.

The wave surface of a wave travelling from a point source of light in an isotropic medium (i.e., a set of points which the wave reaches in time t in the same phase) has the form of a sphere; the direction of the ray coincides with the perpendicular to the wave front, i.e. to the plane tangent to the wave surface at moment t.

In an isotropic medium the phase and the group velocities of the wave can differ in magnitude but they coincide in direction. A *phase*, or *normal*, velocity of the wave $\boldsymbol{v}$ is the velocity of travel of the wave front directed along the perpendicular to it. A *group*, or *ray*, velocity of the wave $\boldsymbol{u}$ is the velocity of the ray, i.e. the velocity of the transmission of energy collinear with the Poynting vector $\boldsymbol{S}$. In an isotropic medium vectors $\boldsymbol{v}$ and $\boldsymbol{u}$ are collinear. In an anisotropic medium they may appear to be non-collinear. To wit, if the directions of vectors $\boldsymbol{E}$ and $\boldsymbol{D}$ in an electromagnetic wave are different, the directions of vectors $\boldsymbol{s}$ and $\boldsymbol{m}$ will also be different (and will make up the same angle). Indeed, from the definition of the Poynting vector (36.1) it is evident that vectors $\boldsymbol{E}$, $\boldsymbol{H}$ and $\mathbf{s}$, as well as $\boldsymbol{D}$, $\boldsymbol{H}$ and $\boldsymbol{m}$ constitute a right-hand triplet of vectors, but if $\boldsymbol{E}$ and $\boldsymbol{D}$ are non-collinear, the ray $\boldsymbol{s}$ and the normal $\boldsymbol{m}$ to the wave front are also non-collinear, this meaning that these two right-hand triplets do not coincide (Figs 34.1 and 36.1). In this case the velocities—the phase one $\boldsymbol{v}$ and the group one $\boldsymbol{u}$—also have different directions, with angle ψ between them. The group velocity of a light wave or, which is just the same, the velocity of a light ray is

$$u = \frac{v}{\cos\psi} = \frac{v}{\boldsymbol{m}\cdot\boldsymbol{s}}.$$

Thus, it either coincides with the phase velocity both in magnitude and in direction or diverges from the latter in direction and exceeds it in magnitude. The quantity reciprocal of the refractive index for the ray

$$q = u/c \tag{36.2}$$

is connected with the refractive index n by relation

$$nq = \frac{1}{\boldsymbol{m}\cdot\boldsymbol{s}} = \frac{1}{\cos\psi}. \tag{36.3}$$

From (36.1) it is evident that the ray vector is perpendicular to the intensity vectors of the electric and magnetic fields:

$$\boldsymbol{s}\cdot\boldsymbol{E} = 0, \qquad \boldsymbol{s}\cdot\boldsymbol{H} = 0. \tag{36.4}$$

With the aid of this we calculate

$$\boldsymbol{s}\times\boldsymbol{D} = -n\boldsymbol{s}\times(\boldsymbol{m}\times\boldsymbol{H}) = n(\boldsymbol{s}\cdot\boldsymbol{m}\boldsymbol{H} - \boldsymbol{s}\cdot\boldsymbol{H}\boldsymbol{m}) = (n\cos\psi)\boldsymbol{H},$$

$$\boldsymbol{s}\times\boldsymbol{H} = n\boldsymbol{s}\times(\boldsymbol{m}\times\boldsymbol{E}) = n(\boldsymbol{s}\cdot\boldsymbol{E}\boldsymbol{m} - \boldsymbol{s}\cdot\boldsymbol{m}\boldsymbol{E}) = -(n\cos\psi)\boldsymbol{E}.$$

These relations very much remind Maxwell's equations, given in Sec. 34 for a plane light wave (34.9). For greater clarity we shall

somewhat transform them and write them out together with (34.9), with the addition of corresponding mater equations ($\varkappa$ is the permittivity tensor for the same frequency ω):

Maxwell's equations

for a light wave		for a light ray	
$n\boldsymbol{m} \times \boldsymbol{H} = -\boldsymbol{D}$,		$q\boldsymbol{s} \times \boldsymbol{H} = -\boldsymbol{E}$,	
$n\boldsymbol{m} \times \boldsymbol{E} = \boldsymbol{H}$,	(34.9)	$q\boldsymbol{s} \times \boldsymbol{D} = \boldsymbol{H}$,	(36.5)
$\boldsymbol{E} = \eta \cdot \boldsymbol{D}$,	(34.2)	$\boldsymbol{D} = \varkappa \cdot \boldsymbol{E}$.	(36.6)

Thus, after a substitution in a transparent non-magnetic crystal the system of equations for a wave changes into the system of equations for a ray

$$\boldsymbol{E} \to \boldsymbol{D}, \quad \boldsymbol{D} \to \boldsymbol{E}, \quad \boldsymbol{H} \to \boldsymbol{H}, \quad \boldsymbol{m} \to \boldsymbol{s}, \quad n \to q, \quad \eta \to \varkappa. \tag{36.7}$$

This allows to obtain quite formally—by simple substitution (36.7) any relations for rays from corresponding relations for waves (and vice versa).

The principle of duality states: any relation valid for quantities $\boldsymbol{E}$, $\boldsymbol{D}$, $\boldsymbol{H}$, $\boldsymbol{m}$, n, η or $\boldsymbol{D}$, $\boldsymbol{E}$, $\boldsymbol{H}$, $\boldsymbol{s}$, q, $\varkappa$ holds upon substitution of quantities in accordance with (36.7).

The role played by optical indicatrices for light waves is performed by the *Fresnel ellipsoid*

$$\boldsymbol{r} \cdot \varkappa \cdot \boldsymbol{r} = 1, \quad \varkappa_{ik} x_i x_k = 1 \tag{36.8}$$

which is the characteristic surface (indicatrix) of the dielectric permittivity tensor.

In isotropic bodies and the cubic system crystals Fresnel's ellipsoid is a sphere of radius $q = 1/n = 1/\sqrt{\varkappa}$.

For uniaxial crystals Fresnel's ellipsoid is an ellipsoid of revolution. In the crystal-physical system of coordinates its equation is

$$N_o^2 (x_1^2 + x_2^2) + N_e^2 x_3^2 = 1 \tag{36.9}$$

(the squares of the principal refractive indices are reciprocal of the eigenvalues of tensor η, and, consequently, are equal to the eigenvalues of the latter reciprocal tensor $\varkappa$). The ellipsoid of revolution has one circular section perpendicular to the principal optic axis of the crystal.

For the uniaxial optically positive crystals Fresnel's ellipsoid is oblate, for the negative crystals it is prolate (Fig. 36.2).

For biaxial crystals it is a triaxial ellipsoid with two circular sections (Fig. 36.3). In a system of coordinates constructed on the eigenvectors of electric tensors, its equation is

$$N_1^2 x_1^2 + N_2^2 x_2^2 + N_3^2 x_3^2 = 1 \tag{36.10}$$

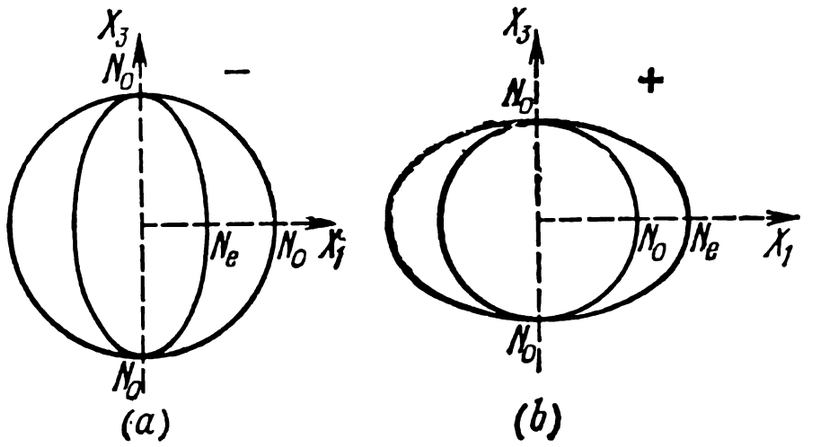


Fig. 36.2. Surfaces of refractive indices in uniaxial crystals: (a) optically negative, (b) optically positive

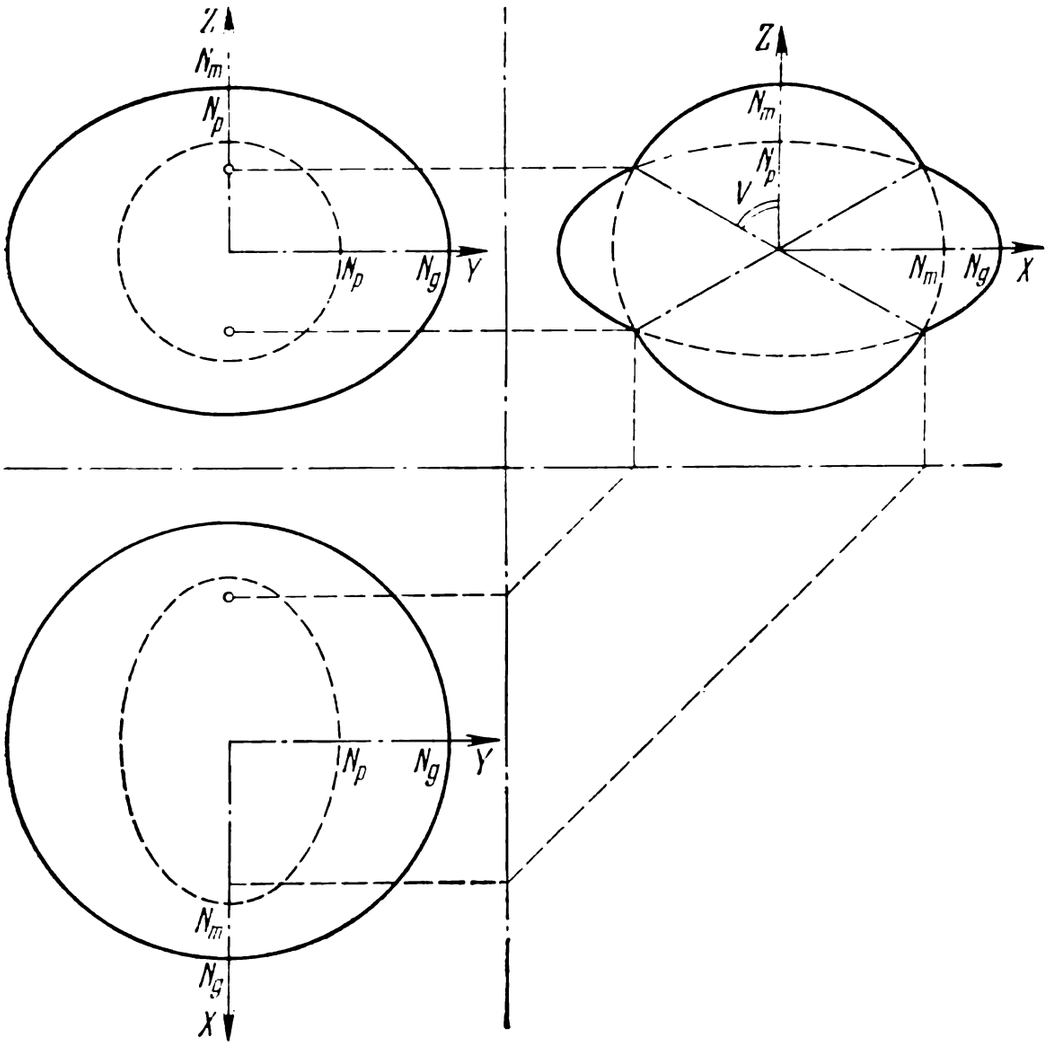


Fig. 36.3. Surfaces of refractive indices in biaxial crystals, in three projections

The principal axes of the optical indicatrix and of the Fresnel ellipsoid for monochromatic light of one and the same frequency always coincide, because mutually reciprocal tensors have the same eigenvectors.

To find the velocities and polarizations of rays propagating in a crystal in direction $\boldsymbol{s}$, it is necessary to consider the central section of Fresnel's ellipsoid by a plane perpendicular to the direction of rays. In a general case this section is an ellipse. Then two rays polarized in two mutually perpendicular directions propagate in the given direction with different velocities and with different wave normals. The lengths of the principal semi-axes of the ellipse, $q_{(1)}$ and $q_{(2)}$ are proportional to these velocities:

$$u_{(1)} = q_{(1)}c, \quad u_{(2)} = q_{(2)}c, \tag{36.11}$$

while the directions of the principal semi-axes coincide with the directions of the electric field intensity vectors $\boldsymbol{E}^{(1)}$ and $\boldsymbol{E}^{(2)}$. If the direction $\boldsymbol{s}$ happens to be perpendicular to the circular central section of Fresnel's ellipsoid, a ray of natural light can propagate in this direction with a velocity u defined by the radius q of this circular section: $u = qc$. In isotropic bodies and cubic crystals $q = 1/n$, in uniaxial crystals $q = 1/N_o$, in biaxial ones $q = 1/N_m$. The directions perpendicular to the circular sections of Fresnel's ellipsoid are called *ray optic axes* or *biradials*. In uniaxial crystals biradials coincide with binormals, in biaxial ones they do not coincide but lie in the same plane of the optic axes.

In practical calculations of the velocities and polarizations of rays it is convenient to use a special system of coordinates with axis X_3 directed along the ray and axes X_1 and X_2 perpendicular to the ray. Upon calculating the required components of the permittivity tensor $\boldsymbol{\varkappa}$ in this system of coordinates quantities $q_{(1)}$ and $q_{(2)}$, and the ray velocities will be readily found from equation

$$\begin{vmatrix} \varkappa_{11} - q^{-2} & \varkappa_{12} \\ \varkappa_{12} & \varkappa_{22} - q^{-2} \end{vmatrix} = 0 \tag{36.12}$$

and from (36.11) respectively. The direction of vector $\boldsymbol{E}^{(1)}$ is determined with the aid of either of the equations

$$\begin{aligned} (\varkappa_{11} - q_{(1)}^{-2})\, E_1^{(1)} + \varkappa_{12} E_2^{(1)} = 0, \\ \varkappa_{12} E_1^{(1)} + (\varkappa_{22} - q_{(1)}^{-2})\, E_2^{(1)} = 0, \end{aligned} \tag{36.13}$$

and vector $\boldsymbol{E}^{(2)}$ is perpendicular to it.

We wish to emphasize that the mutual relations between waves and rays, expressed by substitutions (36.7), occur only within a crystal but not on its surface. Since the boundary conditions for vectors $\boldsymbol{D}$ and $\boldsymbol{E}$ are entirely different, the reflection and refraction of light rays on the surface of a crystal differ essentially from their reflection and refraction within a crystal.

Sec. 37. Solution of the Problem of Light Propagation in a Crystal in an Arbitrary System of Coordinates

The problem of propagation of plane electromagnetic waves in an anisotropic medium is so important that it is expedient to consider its solution in an entirely arbitrary Cartesian system of coordinates connected neither with the direction of light propagation nor with the principal axes of the optical indicatrix.

Let $\boldsymbol{m}$ be the unit vector of a normal to the front of a plane electromagnetic wave of a certain frequency ω, and $\boldsymbol{\eta} = \boldsymbol{\eta}(\omega)$ be the dielectric impermeability tensor for the given frequency. In an arbitrary Cartesian system of coordinates the optical indicatrix equation is as follows:

$$\eta_{ik}x_i x_k = 1, \quad \boldsymbol{r}\cdot\boldsymbol{\eta}\cdot\boldsymbol{r} = 1, \tag{37.1}$$

while the equation of a plane passing through its centre parallel to the wave front is

$$m_i x_i = 0, \quad \boldsymbol{m}\cdot\boldsymbol{r} = 0. \tag{37.2}$$

The section of the optical indicatrix by this plane is an ellipse; all of its points satisfy the two equations. The directions and lengths of the principal semi-axes of this ellipse respectively coincide with the directions of vibrations and the refractive indices of electromagnetic waves having a given normal ($\boldsymbol{m}$) and propagating in the given crystal.

The lengths of the principal semi-axes of the ellipse are the maximum and minimum distances of the points of the ellipse from its centre. Therefore the refractive indices and the directions of vibrations can be found by finding the distances between the centre of the ellipse and the points most and least removed from it, and the directions from the centre in which these points are located.

The radius-vector of any point $\boldsymbol{r} = x_i\boldsymbol{e}_i$ can be written as

$$\boldsymbol{r} = n\boldsymbol{p}, \quad x_i = np_i, \tag{37.3}$$

where n is the length of this vector and $\boldsymbol{p}$ is the unit vector of the same direction:

$$\boldsymbol{p}\cdot\boldsymbol{p} = 1, \quad p_i p_i = 1. \tag{37.4}$$

Then the equation of the optical indicatrix (37.1) will appear as

$$n^2\eta_{ik}p_i p_k = 1, \quad n^2\boldsymbol{p}\cdot\boldsymbol{\eta}\cdot\boldsymbol{p} = 1.$$

For points of the ellipse unit vector $\boldsymbol{p}$ satisfies the equation

$$m_i p_i = 0, \quad \boldsymbol{m}\cdot\boldsymbol{p} = 0. \tag{37.5}$$

Thus the distance of any point of the optical indicatrix from its centre is equal to

$$n = \frac{1}{\sqrt{\eta_{ik} p_i p_k}} = \frac{1}{\sqrt{\boldsymbol{p} \cdot \boldsymbol{\eta} \cdot \boldsymbol{p}}}, \tag{37.6}$$

where $\boldsymbol{p}$ is the unit vector showing in which direction from the centre the point is located. If, however, this point belongs to the ellipse, the components p_i of the unit vector $\boldsymbol{p}$ must also satisfy relation (37.5).

Function $n^{-2}(\boldsymbol{p})$ attains its extreme values for the same values of p_i as function $n(\boldsymbol{p})$, but it is much more convenient for investigation than the latter. Thus the problem is this: for what values of p_i the extreme values of the function

$$\frac{1}{n^2(p_1, p_2, p_3)} = \eta_{ik} p_i p_k \tag{37.7}$$

are attained under additional conditions

$$\Phi_1(p_1, p_2, p_3) = p_i p_i - 1 = 0,$$
$$\Phi_2(p_1, p_2, p_3) = m_i p_i = 0,$$

and what are these values?

To solve this problem, we use Lagrange's multipliers. Let us compose a function

$$F(p_1, p_2, p_3) = \frac{1}{2}\frac{1}{n^2} - \frac{1}{2}\lambda\Phi_1 + \mu\Phi_2 =$$
$$= \frac{1}{2}\eta_{ik} p_i p_k - \frac{1}{2}\lambda(p_i p_i - 1) + \mu m_i p_i, \tag{37.8}$$

where λ and μ are Lagrange's multipliers. Vectors $\boldsymbol{p}^{(q)}$ "doubtful as to the extremums" and values $\lambda_{(q)}$ and $\mu_{(q)}$ corresponding to them will be found from a set of equations

$$\begin{aligned} \frac{\partial F}{\partial p_i} &= \eta_{ik} p_k - \lambda p_i + \mu m_i = 0, \\ \frac{\partial F}{\partial \boldsymbol{p}} &= \boldsymbol{\eta} \cdot \boldsymbol{p} - \lambda \boldsymbol{p} + \mu \boldsymbol{m} = 0, \end{aligned} \tag{37.9}$$

together with (37.4) and (37.5). Equations (37.9) together with (37.5) constitute a set of homogeneous linear equations with respect to the unknown quantitites p_1, p_2, p_3, μ:

$$\begin{aligned} (\eta_{11} - \lambda) p_1 + \eta_{12} p_2 + \eta_{13} p_3 + m_1 \mu &= 0, \\ \eta_{21} p_1 + (\eta_{22} - \lambda) p_2 + \eta_{23} p_3 + m_2 \mu &= 0, \\ \eta_{31} p_1 + \eta_{32} p_2 + (\eta_{33} - \lambda) p_3 + m_3 \mu &= 0, \\ m_1 p_1 + m_2 p_2 + m_3 p_3 &= 0. \end{aligned} \tag{37.10}$$

A set of homogeneous linear equations is known to have non-trivial, i.e. not identically equal to zero, solutions, if and only if

the determinant of the set is zero:

$$\begin{vmatrix} \eta_{11}-\lambda & \eta_{12} & \eta_{13} & m_1 \\ \eta_{21} & \eta_{22}-\lambda & \eta_{23} & m_2 \\ \eta_{31} & \eta_{32} & \eta_{33}-\lambda & m_3 \\ m_1 & m_2 & m_3 & 0 \end{vmatrix} = 0. \tag{37.11}$$

Condition (37.11) is a quadratic equation with respect to Lagrange's multiplier λ. It can be easily proved that its roots $\lambda_{(1)}$ and $\lambda_{(2)}$ are real (see (37.18)). Substituting one of the roots, say, $\lambda_{(1)}$, into system (37.10) we find the corresponding values of the components of vector $\boldsymbol{p}^{(1)}$ and of Lagrange's multiplier μ_1 up to normalization, i.e. the values of $\alpha p_1^{(1)}$, $\alpha p_2^{(1)}$, $\alpha p_3^{(1)}$ and $\alpha\mu$. The unknown coefficient α will be found from (37.4), whereupon vector $\boldsymbol{p}^{(1)}$ and Lagrange's multiplier $\mu_{(1)}$ will be determined up to their signs, if only $\lambda_{(1)} \neq \lambda_{(2)}$. This accuracy is quite sufficient, since the centre of the ellipse serves as its centre of symmetry and therefore $n\,(-\boldsymbol{p}) = n\,(\boldsymbol{p})$.

Let us discuss some general characteristics of the solution of this problem. By scalar multiplication of both parts of second equation (37.9) by vector $\boldsymbol{p}^{(q)}$ where $q = 1, 2$, we obtain

$$\lambda_{(q)} = \boldsymbol{p}^{(q)} \cdot \boldsymbol{\eta} \cdot \boldsymbol{p}^{(q)}. \tag{37.12}$$

Thus Lagrange's multiplier $\lambda_{(q)}$ is equal to the normal component of the dielectric impermeability tensor in the direction of vibrations. It follows from (37.7) that this multiplier is simply equal to the inverse value of the square of the refractive index of the light wave with the given direction of vibrations:

$$\lambda_{(q)} = n_{(q)}^{-2}. \tag{37.13}$$

By scalar multiplication of both parts of the second equation (37.9) by vector $\boldsymbol{m}$, we obtain

$$\mu_{(q)} = -\boldsymbol{m} \cdot \boldsymbol{\eta} \cdot \boldsymbol{p}^{(q)}. \tag{37.14}$$

Thus Lagrange's multiplier $\mu_{(q)}$ taken with a reverse sign is equal to the impermeability tensor tangential component in the direction of vibrations $\boldsymbol{p}$ and wave normal $\boldsymbol{m}$. Since tangential components of an isotropic tensor are zero, Lagrange's multiplier $\mu_{(q)}$ differs from zero only in optically anisotropic crystals. Insofar as the unit vector $\boldsymbol{p}^{(q)}$ of the direction of vibrations is collinear with the induction vector $\boldsymbol{D}^{(q)}$ of the electromagnetic wave with a normal $\boldsymbol{m}$ and velocity $c/n_{(q)}$, vector $\boldsymbol{\eta} \cdot \boldsymbol{p}^{(q)}$ is collinear with the vector of the electric field intensity $\boldsymbol{E}^{(q)}$ of this wave. Multiplier $\mu_{(q)}$ is equal (taken with the reversed sign) to the projection of vector $\boldsymbol{\eta} \cdot \boldsymbol{p}^{(q)}$ onto the direction of the wave normal. Thus it shows how much the vector of the electric field of the given light wave diverges from the plane

of the wave front. The divergence is possible only when light propagates in an optically anisotropic medium.

Equations (37.10) and (37.11) are somewhat simplified in a system of coordinates constructed on the eigenvectors of the dielectric impermeability tensor η. In this system of coordinates equation (37.11) is expressed in the following form:

$$\lambda^2 - [(\eta_{(2)} + \eta_{(3)})\, m_1^2 + (\eta_{(3)} + \eta_{(1)})\, m_2^2 + (\eta_{(1)} + \eta_{(2)})\, m_3^2]\, \lambda + \\ + [\eta_{(2)}\eta_{(3)} m_1^2 + \eta_{(3)}\eta_{(1)} m_2^2 + \eta_{(1)}\eta_{(2)} m_3^2] = 0. \qquad (37.15)$$

Having calculated the roots of this quadratic equation $\lambda_{(1)}$ and $\lambda_{(2)}$ we find vectors $\boldsymbol{p}^{(1)}$ and $\boldsymbol{p}^{(2)}$ of the directions of vibrations and, if necessary, Lagrange's multipliers $\mu_{(1)}$ and $\mu_{(2)}$ from equations (37.10) which in the proper system of tensor η are as follows:

$$\begin{gathered} (\eta_{(1)} - \lambda_{(q)})\, p_1^{(q)} + m_1 \mu_{(q)} = 0, \\ (\eta_{(2)} - \lambda_{(q)})\, p_2^{(q)} + m_2 \mu_{(q)} = 0, \\ (\eta_{(3)} - \lambda_{(q)})\, p_3^{(q)} + m_3 \mu_{(q)} = 0, \\ m_1 p_1^{(q)} + m_2 p_2^{(q)} + m_3 p_3^{(q)} = 0 \\ (q = 1,\ 2). \end{gathered} \qquad (37.16)$$

However, equations (37.10) and (37.11) can be much more essentially simplified by writing them down in a system of coordinates one of whose axes, say, X_3, is directed along the vector of the wave normal $\boldsymbol{m}$. In this system of coordinates $m_1 = m_2 = 0$, $m_3 = 1$, and only components p_1 and p_2 of the vector of the direction of vibrations differ from zero. Of the four equations of (37.10) there remain, in essence, only two

$$\begin{gathered} (\eta_{11} - \lambda)\, p_1 + \eta_{12} p_2 = 0, \\ \eta_{21} p_1 + (\eta_{22} - \lambda)\, p_2 = 0. \end{gathered} \qquad (37.17)$$

The determinant of this system of homogeneous linear equations is equal to zero only when

$$\lambda_{(1,\,2)} = \frac{1}{2}\left[(\eta_{11} + \eta_{22}) \pm \sqrt{(\eta_{11} - \eta_{22})^2 + (2\eta_{12})^2}\right]. \qquad (37.18)$$

Substituting λ_1 into equations (37.17) we find the components of vector $\boldsymbol{p}^{(1)}$. Thereupon with the aid of the third equation of (37.10) we can find

$$\mu_{(1)} = -\eta_{31} p_1^{(1)} - \eta_{32} p_2^{(1)}. \qquad (37.19)$$

Vector $\boldsymbol{p}^{(2)}$ and Lagrange's multiplier $\mu_{(2)}$ are found similarly.

Sec. 38. Fresnel's Equation. Wave and Ray Surfaces

In Sec. 37 it was shown that in an arbitrary, in particular in a crystal-physical, system of coordinates equation (37.11) for determining the refractive indices of waves propagating in the direction $\boldsymbol{m}$ is

$$\begin{vmatrix} \eta_{11}-n^{-2} & \eta_{12} & \eta_{13} & m_1 \\ \eta_{21} & \eta_{22}-n^{-2} & \eta_{23} & m_2 \\ \eta_{31} & \eta_{32} & \eta_{33}-n^{-2} & m_3 \\ m_1 & m_2 & m_3 & 0 \end{vmatrix} = 0. \qquad (38.1)$$

Here n is the refractive index, and m_1, m_2, m_3 are the components of the unit vector of the wave normal $\boldsymbol{m}$. In a system of coordinates constructed on the eigenvectors of the dielectric tensors this equation (after multiplication of both its parts by $n^4N_1^2N_2^2N_3^2$) is written as

$$n^4(N_1^2m_1^2+N_2^2m_2^2+N_3^2m_3^2)-n^2[N_1^2(N_2^2+N_3^2)m_1^2+ \\ +N_2^2(N_3^2+N_1^2)m_2^2+N_3^2(N_1^2+N_2^2)m_3^2]+N_1^2N_2^2N_3^2=0 \qquad (38.2)$$

and is called *Fresnel's equation*. It determines the refractive index n as a function of the unit vector of the wave normal $\boldsymbol{m}$.

If intercepts of length n ($\boldsymbol{m}$) are marked off from the origin in all directions $\boldsymbol{m}$, there will result a two-sheet (since two values n correspond to almost every vector $\boldsymbol{m}$) surface of refractive indices. Its equation in polar coordinates is obtained from Fresnel's equation (38.2) by means of substitution

$$m_1 = \cos\varphi\sin\vartheta, \quad m_2 = \sin\varphi\sin\vartheta, \quad m_3 = \cos\vartheta, \qquad (38.3)$$

and in Cartesian coordinates by substitution

$$nm_1 = x_1, \quad nm_2 = x_2, \quad nm_3 = x_3, \quad n^2 = x_1^2+x_2^2+x_3^2. \qquad (38.4)$$

This surface is also called the *surface of wave vectors*: if wave vectors of all light waves of a given frequency propagating in a crystal are marked off from a single point, the ends of the vectors will form a surface similar to the surface of the refractive indices, since the lengths of the wave vectors are proportional to the refractive indices of the respective waves. For optically isotropic media this surface is a sphere.

For uniaxial crystals Fresnel's equation (38.2) is reduced to

$$(n^2-N_o^2)\{n^2[N_o^2(m_1^2+m_2^2)+N_e^2m_3^2]+N_o^2N_e^2\}=0. \qquad (38.5)$$

With the aid of substitution (38.4) we derive now the equation of the surface of refractive indices for uniaxial crystals:

$$(x_1^2+x_2^2+x_3^2-N_o)[N_o^2(x_1^2+x_2^2)+N_e^2x_3^2-N_o^2N_e^2]=0. \qquad (38.6)$$

This is a double surface which decomposes into a sphere

$$x_1^2 + x_2^2 + x_3^2 = N_0^2$$

and an ellipsoid of revolution

$$\frac{x_1^2 + x_2^2}{N_e^2} + \frac{x_3^2}{N_0^2} = 1.$$

Apparently, a light wave in a crystal of the intermediate category breaks up into an ordinary wave, for which the velocity and the re-

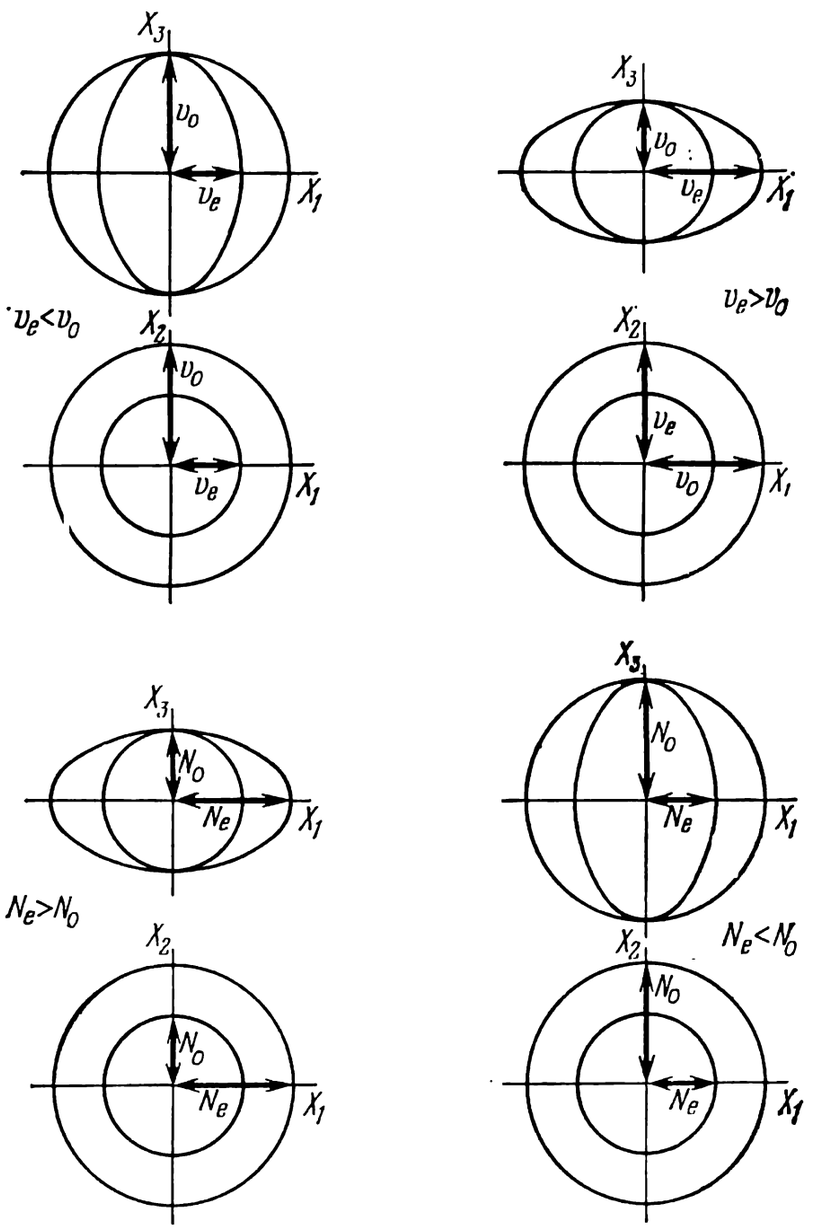


Fig. 38.1. Sections of the surfaces of refractive indices and wave velocities for optically uniaxial crystals

fractive index $n_0 = N_0$ do not depend on the direction, and an extraordinary wave, for which the refractive indices n_e are different in different directions (Fig. 38.1).

The sphere and the ellipsoid contact each other in two points which determine the direction of the optic axis coinciding with the principal symmetry axis of the crystal. We should remember that in optically uniaxial crystals the principal symmetry axis is the optic axis of the crystal and at the same time a binormal (i.e. a perpendicular to the circular section of the optical indicatrix) and a biradial (i.e. a perpendicular to the circular section of Fresnel's ellipsoid). A wave travelling along the optic axis does not experience birefringence. Crystals of the intermediate category are optically uniaxial. As has already been mentioned, uniaxial crystals are considered optically positive, if $N_e > N_o$, i.e. if the sphere is inscribed into the ellipsoid, and optically negative if $N_e < N_o$, i.e. if the ellipsoid is inscribed into the sphere.

The examination of Fresnel's general equation (38.2) makes it possible to define the kind of the surface of refractive indices of biaxial crystals. The equation of this surface in Cartesian coordinates is as follows:

$$(x^2+y^2+z^2)(N_p^2x^2+N_m^2y^2+N_g^2z^2)-N_p^2(N_m^2+N_g^2)x^2-$$
$$-N_m^2(N_g^2+N_p^2)y^2-N_g^2(N_p^2+N_m^2)z^2+N_p^2N_m^2N_g^2=0. \quad (38.7)$$

This reveals the comparative magnitude of the principal refractive indices. The analysis of this surface of the fourth degree in its general form is difficult, therefore we shall first consider the sections of the surface by the coordinate planes. Its section by plane $z = 0$ is characterized by the equation

$$(x^2+y^2-N_g^2)(N_p^2x^2+N_m^2y^2-N_p^2N_m^2)=0, \quad (38.8)$$

which shows that this section consists of a circumference $x^2 + y^2 = N_g^2$ and an ellipse $\frac{x^2}{N_m^2}+\frac{y^2}{N_p^2}=1$, the ellipse being inside the circumference.

The section of the refractive indices surface by plane $x = 0$ also consists of a circumference $y^2 + z^2 = N_p^2$ and an ellipse $\frac{y^2}{N_g^2}+\frac{z^2}{N_m^2}=1$, but in this case the circumference is inside the ellipse.

Finally, as regards section $y = 0$, the circumference $x^2 + z^2 = N_m^2$ and the ellipse $\frac{x^2}{N_g^2}+\frac{y^2}{N_p^2}=1$ intersect each other.

Their common points are the points of intersection of the refractive indices surface by the optic axes, i.e. by the binormals of the optical indicatrix. (Let us recall that in biaxial crystals the binormals and biradials do not coincide in direction, see Sec. 36.) The sections are shown in Fig. 38.2.

The reciprocity between waves and rays, discussed in Sec. 36, allows obtaining similar results for rays too. Using the substitution (36.7) we shall write in an arbitrary system of coordinates an equation for determining the squares of the ray refractive indices of light rays propagating in the direction of unit vector s with the components s_1, s_2, s_3:

$$\begin{vmatrix} \varkappa_{11}-q^{-2} & \varkappa_{12} & \varkappa_{13} & s_1 \\ \varkappa_{21} & \varkappa_{22}-q^{-2} & \varkappa_{23} & s_2 \\ \varkappa_{31} & \varkappa_{32} & \varkappa_{33}-q^{-2} & s_3 \\ s_1 & s_2 & s_3 & 0 \end{vmatrix} = 0. \qquad (38.9)$$

In the system of coordinates constructed on the eigenvectors of the dielectric tensors η (ω) and $\varkappa$ (ω), the equation (after multiplication by q^4) becomes

$$q^4 (N_2^2 N_3^2 s_1^2 + N_3^2 N_1^2 s_2^2 + N_1^2 N_2^2 s_3^2) - q^2 [(N_2^2 + N_3^2) s_1^2 + (N_3^2 + N_1^2) s_2^2 + (N_1^2 + N_2^2) s_3^2] + 1 = 0. \qquad (38.10)$$

Using substitutions (38.3) or (38.4) now obtain an equation of the *ray surface* (which is sometimes called the wave surface); in Cartesian coordinates it is

$$(x_1^2 + x_2^2 + x_3^2)(N_2^2 N_3^2 x_1^2 + N_3^2 N_1^2 x_2^2 + N_1^2 N_2^2 x_3^2) - (N_2^2 + N_3^2) x_1^2 - (N_3^2 + N_1^2) x_2^2 - (N_1^2 + N_2^2) x_3^2 + 1 = 0. \qquad (38.11)$$

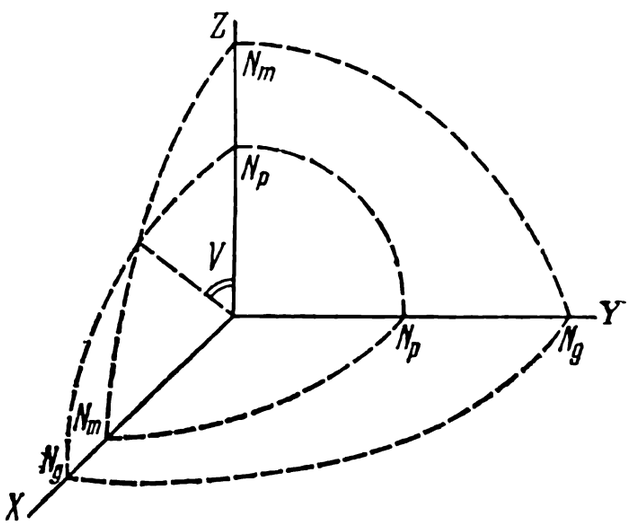


Fig. 38.2. Sections of the refractive indices surface in a biaxial crystal by the coordinate planes

Since the ray velocity u is proportional to quantity q, the ray surface may be lucidly imagined as a wave front emitted from a point source of light located in the centre of the surface. Since in every direction not coinciding with the biradial two mutually perpendicularly polarized rays propagate with different velocities, this is a two-sheet surface. In appearance it resembles the surface of refractive indices, but there is a difference between them: the refractive indices surface cuts off intercepts N_o, N_e, or N_g, N_m, N_p on the coordinate axes, while the ray surface cuts off intercepts $1/N_o$, $1/N_e$, or $1/N_g$, $1/N_m$, $1/N_p$ on the same axes. Therefore the surfaces are reciprocal. Thus, for a uniaxial negative crystal the refractive indices surface is an ellipsoid of revolution inside a sphere, while the ray surface is a sphere inside ellipsoid (Fig. 38.1). Similar relations hold also for positive uniaxial crystals and for the biaxial ones (see Table 39.1).

Sec. 39. Interconnection Between the Optical Surfaces in Crystals. Conical Refraction

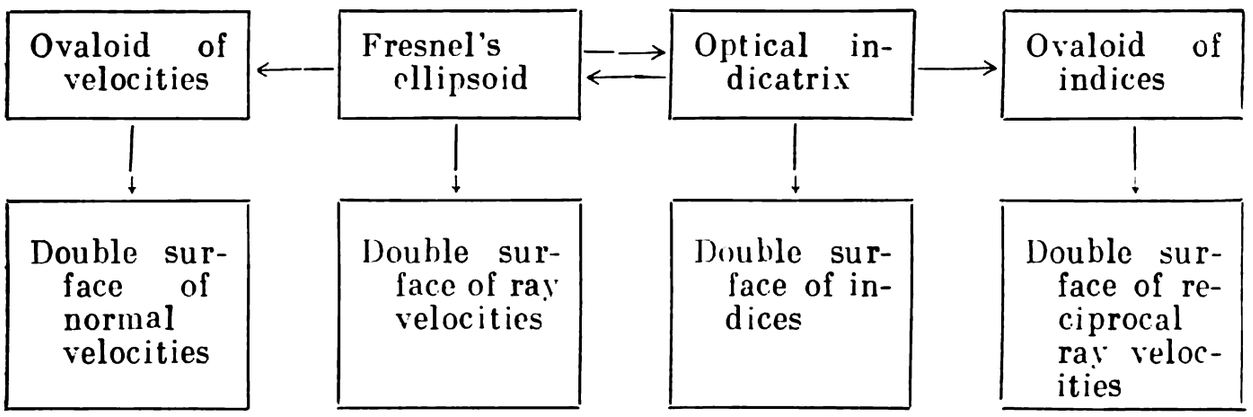
The optical properties of crystals can be characterized by different quantities: by ray or wave velocities or by refractive indices, by the flow of energy or by the propagation of a wave front. The relations between these quantities are defined by the principle of duality. For each of these quantities there can be constructed representation surfaces or indicatrices. Several decades before the Maxwell theory was put forward all these surfaces were constructed by Fresnel on the basis of experimental data obtained by the observation of optical phenomena in crystals in polarized light, and taking account of the crystal symmetry.

A general description of these surfaces is given in Table 39.1.

The form and orientation of all optical surfaces, both ray and normal ones, are connected, according to Neumann's principle, with crystal symmetry and, in the final analysis, always depend on the dielectric permittivity tensor (or the dielectric susceptibility tensor).

The optical phenomena observed in crystals are most often interpreted with the aid of the optical indicatrix, the ray surface and Fresnel's ellipsoid, but in some cases it is convenient to resort to other mutually interconnected surfaces (Pockels, 1906; Shubnikov, 1958).

The scheme of interconnections between surfaces specifying the birefringence of crystals is this:



The relations between these surfaces correspond to the relations between a ray and a normal to a wave front. In an isotropic medium, where the wave front travelling from a point source has the form of a sphere, the ray and the normal to the wave front coincide. In an anisotropic medium the directions of the ray and the normal coincide only along the own directions of dielectric tensors, this causing the difference between the "ray" and "normal" surfaces. For building a wave normal conjugate to a given ray it is necessary to draw a plane tangential to the wave surface at the exit point of the ray and to drop a perpendicular onto this plane from the centre of the surface

Table 39.1

Optical Surfaces of Crystals of the Intermediate and Lower Categories

Optical character of crystals	Wave (ray) surface	Optical indicatrix	Fresnel's ellipsoid	Surface of normals	Surface of refractive indices (surface of wave vectors)	Surface of reciprocal velocities of rays
Uniaxial positive +	Prolate ellipsoid of revolution inside a sphere	Prolate ellipsoid of revolution $N_e > N_o$	Oblate ellipsoid of revolution $v_o > v_e$	Prolate ovaloid of revolution inside a sphere	A sphere inside an oblate ellipsoid of revolution	A sphere inside an oblate ovaloid of revolution
Uniaxial negative —	Sphere inside an oblate ellipsoid of revolution	Oblate ellipsoid of revolution $N_o > N_e$	Prolate ellipsoid of revolution $v_e > v_o$	A sphere inside an oblate ovaloid of revolution	Prolate ellipsoid of revolution inside a sphere	Prolate ovaloid of revolution inside a sphere
Biaxial positive +	Principal sections are formed by circles and ellipses. Biradials pass through points of their intersection	$N_g - N_m > N_m - N_p$	$v_1 - v_2 < v_2 - v_3$	The major axis is bisectrix of the acute angle	The major axis is bisectrix of the acute angle	Principal sections are formed by circles and ovals. Biradials pass through points of their intersection
Biaxial negative —		Ellipsoid with three unequal principal axes	Ellipsoid with three unequal principal axes	Principal sections are formed by circles and ovals. Optic axes pass through points of their intersection	Principal sections are formed by circles and ellipses. Optic axes pass through points of their intersection	
		$N_g - N_m < N_m - N_p$	$v_1 - v_2 > v_2 - v_3$	The major axis is bisectrix of the obtuse angle	The major axis is bisectrix of the obtuse angle	

(Fig. 39.1). The ratio of the lengths of these intercepts is equal to the ratio of the ray and normal (i.e. group and phase) velocities.

Drawing normals m conjugate to each ray s it is possible to construct a surface of normal velocities. If the surface of ray velocities is an ellipsoid, the corresponding surface of normal velocities will be an ovaloid. To the sphere of ray velocities there corresponds a sphere of normal velocities.

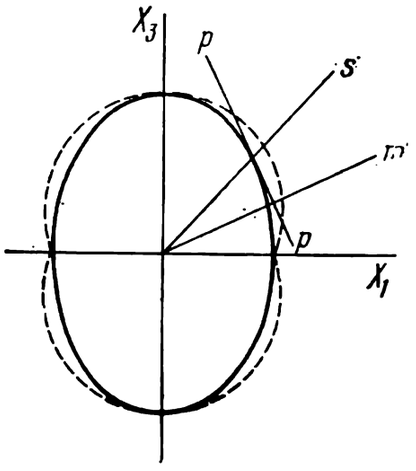


Fig. 39.1. The relation between a ray, a normal to the wave front and sections of the wave surface ellipsoid and normal velocities ovaloid

All these surfaces are derived by simple geometric construction starting from Fresnel's ellipsoid or from the optical indicatrix (see Pockels, 1906). Fig. 39.2 shows the sections of eight surfaces constructed for an imaginary negative crystal with $N_o = 1.86$, $N_e = 1.07$ and with a relative scale for these indices being maintained (Karandeyev, 1913).

The analysis of such surfaces allows to find and to explain all the peculiarities of the refraction and polarization of light in crystals. Thus, comparing the optical indicatrix with a ray surface it is possible to come to a lucid understanding of the difference between the biradials and binormals of an optically biaxial crystal (see Sec. 22). Biradials correspond to the direction with equal group velocities, binormals correspond to the directions with equal phase velocities of a wave.

Biradials are perpendicular to the circular sections of Fresnel's ellipsoid, binormals, to the circular sections of the optical indicatrix. The relation between them is explained in Fig. 39.3 which shows the section of the ray surface and of the surface of normals of a biaxial crystal by plane X_3OX_1. Four points at which the ellipse and the circle intersect determine the direction of biradials RR. Drawing a common tangent to the ellipse and the circle and dropping a normal m onto it we find the points of intersection of the oval (the dotted line) and the circle which determine the directions of binormals.

In practice the ray and normal (phase and group) velocities are so close to each other that the difference between the directions of the binormals and biradials is of no importance, except for the peculiar phenomenon of *conical refraction*.

Two conjugate rays correspond to each binormal in a plane section. Changing from section to space, we can see that a tangential plane PP touches the double surface along a circumference, this meaning that to one direction of the binormal there correspond many conjugate rays that form a hollow cone within a crystal plate and a hollow cylinder upon the emergence from the plate. Therefore, if

a plate is cut out of a biaxial crystal, strictly perpendicularly to one of the crystal's optic axes (binormals), and a narrow beam of natural

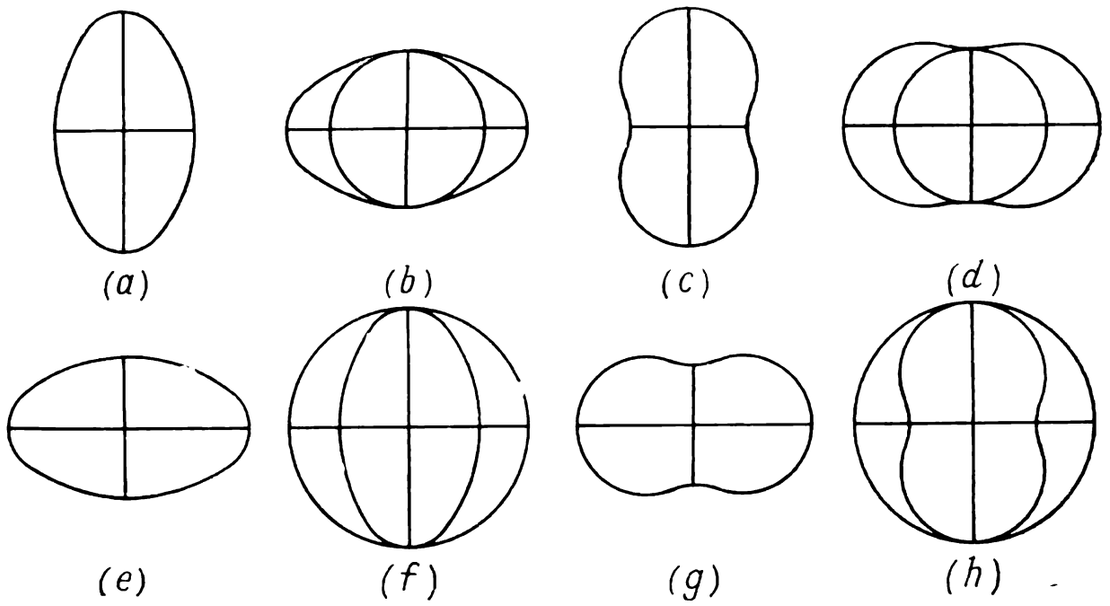


Fig. 39.2. Sections of the optical surfaces of a uniaxial negative crystal by plane X_3X_1: (a) Fresnel's ellipsoid, (b) ray surface, (c) ovaloid of wave velocities, (d) surface of wave normals, (e) optical indicatrix, (f) refractive indices surface, (g) ovaloid of the reciprocal quantities of ray velocities, (h) surface of the reciprocal quantities of ray velocities

light is transmitted along a perpendicular to the plate, the ray will be divided not into two mutually perpendicularly polarized rays, but into an infinite set of rays linearly polarized at different azimuths (Fig. 39.4). A ray of light from a point source will produce not one single point on the screen, as it would have been if it travelled along the optic axis of a uniaxial crystal, and not two points, as it would have been in cases of all other directions in a uniaxial or a biaxial crystal, but will produce a light ring whose diameter will not change upon the removal of the screen to some distance from the crystal plate. The brightness of the ring changes: there is a position of a maximum brightness and a dark strip corresponding to the minimum brightness. If the analyzer is rotated about the direction of the ray, the dark strip will make a full revolution around the ring, thus showing that for different azimuths the rays forming the ring are linearly polarized. This constitutes the phenomenon of *internal conical refraction* (Fig. 39.4).

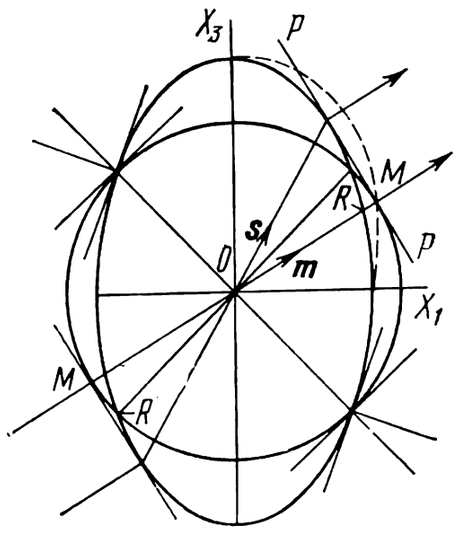


Fig. 39.3. To the explanation of the conical refraction phenomenon and the explanation of the relation between biradials and binormals

An analogous phenomenon of *external conical refraction* consists in the correspondence to a single biradial direction of an infinity of waves the normals to which form a hollow cone. To observe the external conical refraction it is necessary to transmit a ray of light through a plate cut out strictly perpendicularly to a biradial (Fig. 39.5).

It is interesting to note that the discovery of conical refraction is an example of remarkable scientific foresight. It was foretold by

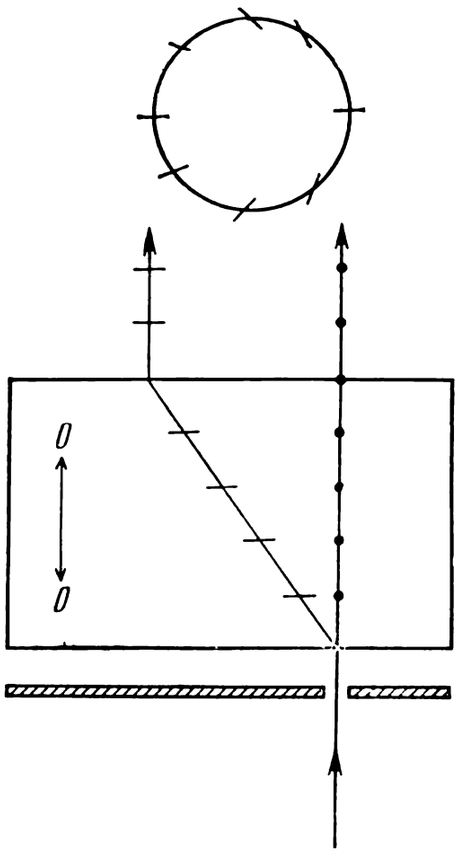


Fig. 39.4. Schematic diagram of the observation of internal conical refraction: *OO*—direction of the optic axis of the crystal. The dots and dashes show the directions of vibrations (Shubnikov, 1958)

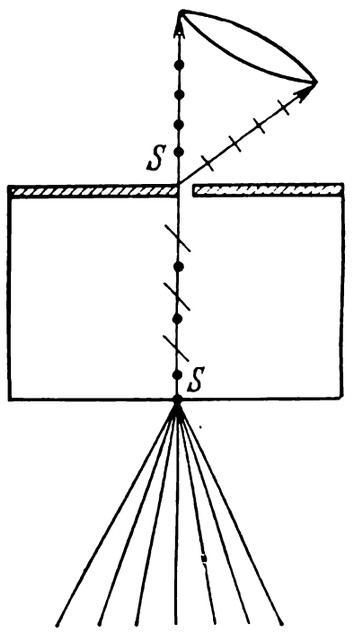


Fig. 39.5. Schematic diagram of the observation of external conical refraction: *SS*—direction of the crystal's biradial. The dots and dashes show the directions of vibrations (Shubnikov, 1958)

William Hamilton in 1832 (Pockels, 1906) merely on the basis of speculative analysis of the form of the wave surface of crystals constructed by Fresnel. Hamilton suggested to Lloyd to verify his conclusion, and indeed, a year later (in 1833) Lloyd described his experimental observation of the internal and external conical refraction in an aragonite crystal.

Aragonite is one of the few substances in which the phenomenon of conical refraction can be seen; for the majority of substances the angle of conical refraction is so small that experimental attempts to see this phenomenon practically fail. As it follows from (38.7)

and (38.11), the angle between an element and the axis of the cone (or, the angle of the cone) of the external conical refraction α is obtained from the relation

$$\tan \alpha = N_p N_g \sqrt{(N_p^{-2} - N_m^{-2})(N_m^{-2} - N_g^{-2})}. \qquad (39.1)$$

Table 39.2 gives the values of the angle α for some substances.

Table 39.2

Angle of the Cone of External Conical Refraction α for Some Substances

Substance	α	Substance	α
Aragonite	1°52′	Sugar	0°52′
Sulphur	7°11′	Gypsum	0°18′
Tartaric acid	3°54′	Mica	0°59′
Barite	0°15′	Topaz	0°16′

Perkalskis (1980) made an excellent demonstration of conical refraction with the aid of a laser beam.

In conclusion we wish to note that because of the scatter of the values of η, the forms of optical surfaces depend on the frequency of the electromagnetic wave incident on the crystal (see Sec. 40).

Sec. 40. Observation of the Optical Anisotropy of Crystals in Polarized Light

It is necessary to know the optical surfaces listed in Table 39.1 to explain the optical phenomena observed in crystals in polarized light.

The observation of crystals in polarized light is done with the aid of a polarizing microscope or polarizing set-ups arranged as shown in Fig. 40.1. Polaroids,

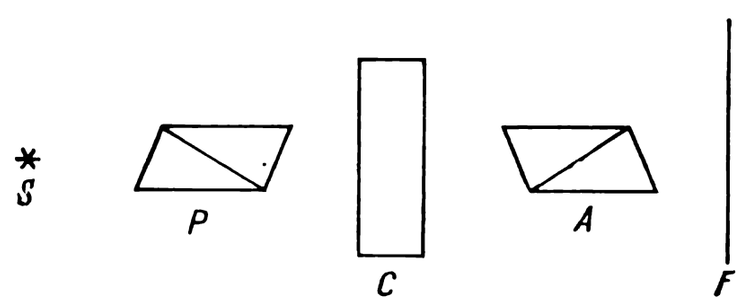


Fig. 40.1. Diagram of the observation of crystals in parallel polarized light. S—source of light, P—polarizer, A—analyzer, C—crystal plate, F—screen

nicols or other polarizing prisms are used as a polarizer and an analyzer. When the method of convergent light is used (see below), two condensers are inserted into the set-up.

A beam of natural light passing through the polarizer becomes plane-polarized and next, entering the observed crystal plate it experiences birefringence,

the polarization planes of the two resulting rays being determined by the symmetry planes of the optical indicatrix of the crystal under observation and by their orientation with respect to the incident beam. The polarizer is meant not so much for the polarization of light, as for the creation of the coherence of vibrations getting into the crystal plate. The two rays resulting from the breaking-up of the plane-polarized beam are coherent and therefore can develop interference. In passing through the crystal plate these two rays acquire a path-length difference retardation:

$$\Delta = d(n_1 - n_2), \tag{40.1}$$

where d is the thickness of the plate, n_1, n_2 are the refractive indices of the two rays which in a general case travel through the crystal in non-parallel courses with a path-length difference. On their exit from the plate the rays again become parallel, and if the beam of light is sufficiently wide, and the plate is sufficiently thin, they can travel in the same direction overlapping each other.

The rays that passed through the polarizer and the crystal plate are parallel, coherent and have a path-length difference, but for their interference their polarization planes must coincide. This is what the analyzer is for: it brings the vibrations of the two rays into a single plane. To be more exact, the analyzer selects those vibration components which lie in the plane of its polarization.

In the absence of a crystal plate the intensity of light that leaves the optical system is defined by the Malus law

$$I = I_0 \cos^2 \alpha; \tag{40.2}$$

here α is the angle between the polarization planes of the polarizer and analyzer, I_0 is the intensity of light that passed through the polarizer. If $\alpha = 0$, the nicols are parallel and a maximum intensity of transmitted light is observed. If $\alpha = 90°$, the nicols are "crossed" * (the polarization planes of the polarizer and analyzer are mutually perpendicular), light does not pass through the optical system, the field of vision is dark.

If however a birefringent crystal plate is placed between crossed nicols, the field of vision becomes brighter. The brightness depends on the magnitude of birefringence, and the latter in its turn on the optical constants of the crystal, on its orientation in respect of the optic axis of the system and on the thickness of the crystal plate.

The phenomenon of the birefringence of light in crystals is fairly weak in itself. It can be directly observed only in some very strongly birefringent crystals, such as calcite (Iceland spar) and saltpetre. The interference of polarized light creates conditions due to which the birefringence is strongly displayed as *chromatic (coloured) polarization of light in crystals*: as a result of the interference of the rays passing through a crystal plate, thin plates in polarized light will seem in a general case coloured with bright interference colours. The colour itself depends on the path-length difference in the plate, the intensity of colour depends on the orientation of the plate with respect to the polarization planes of the polarizer and analyzer.

A plate cut out of a crystal perpendicularly to its optic axis will appear dark in crossed nicols, just as a plate of optically isotropic substance. If a plane-parallel plate is cut out not perpendicularly to the optic axis of a birefringent crystal, then in monochromatic light it will appear bright, and in white light, coloured.

---

* The terms "crossed nicols" and "parallel nicols" are used by tradition even when not nicols but polaroids or other prisms are used as polarizing devices.

Let P and A in Fig. 40.2 be the directions of vibration in the polarizer and analyzer forming angle γ between themselves, and I and II be the directions of the principal axes of an ellipse, this being the section in which the optical indicatrix of the crystal is cut by the plane of the plate. The axes constitute angles α and $90° - \alpha$ with P, and angles β and $90° - \beta$ with A respectively, $\alpha + \beta + \gamma = 180°$. If OP is the amplitude of the vibrations of light that passed through the polarizer, then OM_1 and OM_2 are the amplitudes of vibrations of light waves propagating within the crystal. We denote the refractive indices of these waves by n_1 and n_2. Having passed through the crystal plate the waves will have a path-length difference:

$$\varphi = \frac{2\pi}{\lambda} d (n_1 - n_2), \qquad (40.3)$$

where λ is the light wavelength in vacuum, and d is the thickness of the plate. In an analyzer the amplitude of these waves decreases to OA_1 and OA_2 respectively but the phase difference between them will remain unchanged. Therefore, the intensity of light that passed through the analyzer is

$$I = (OA_1)^2 + (OA_2)^2 - 2 (OA_1) (OA_2) \cos \varphi. \qquad (40.4)$$

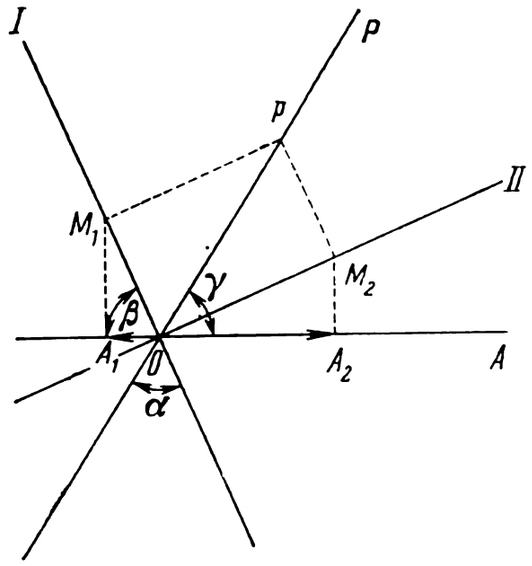


Fig. 40.2. Diagram explaining the origin of phase difference in the transmission of light through a crystal plate.

If the intensity of light coming out of a polarizer is denoted I_0, then $OP = I_0^{1/2}$, $OM_1 = I_0^{1/2} \cos \alpha$, $OM_2 = I_0^{1/2} \sin \alpha$, $OA_1 = I_0^{1/2} \cos \alpha \cos \beta$, $OA_2 = I_0^{1/2} \sin \alpha \sin \beta$. Substituting these values into (40.4) we find upon elementary transformations

$$I = I_0 \cos^2 \gamma + I_0 \sin 2\alpha \sin 2\beta \sin^2 (\varphi/2). \qquad (40.5)$$

In crossed polarized light ($\gamma = 90°$, $\beta = 90° - \alpha$)

$$I = I_0 \sin^2 2\alpha \sin^2 (\varphi/2), \qquad (40.6)$$

and in parallel polarized light ($\gamma = 0$, $\beta = 180° - \alpha$)

$$I = I_0 - I \sin^2 2\alpha \sin^2 (\varphi/2). \qquad (40.7)$$

In crossed polarized light according to the usual condition of interference, those rays will be amplified for which the path-length difference $\Delta = d (n_1 - n_2)$ is equal to an odd number of half-waves. If the crystal plate is in a diagonal position, so that $\sin^2 2\alpha = 1$, the interference phenomena are displayed the strongest, colouring is of a maximum intensity. During a complete rotation of the plate about the direction of the beam of light passing through it, or, in other words, about the optic axis of the polarization scheme, there will be observed four complete extinctions and four maximum brightnesses of colouring.

Since the right-hand sides of expressions (40.6) and (40.7) total up to I_0, with parallel nicols the colouring will be supplementary: in a diagonal position the plate will be bright in supplementary colours, while during a complete rotation there will be observed four positions when it will appear white. Colouring depends on the thickness and orientation of the plate.

The observation of crystals in parallel polarized light is used for measuring the birefringence, the thickness of a crystal, and in mineralogical and petrographical practice for diagnosing crystals, especially in rocks.

The examination of crystals in convergent polarized light allows to determine the orientation and character of the optical indicatrix, to measure the angle between the optic axes of a biaxial crystal, to determine the optic sign of the crystal, to reveal the dispersion of the optic axes and the rotation of the polarization plane, to determine qualitatively and quantitatively the change of the optical indicatrix under external influences (see piezooptical and electrooptical effects, Sec. 77).

The diagram of a set-up for the observation of a crystal in convergent polarized light is shown in Fig. 40.3. Besides polarizer P, analyzer A, and crystal C, an

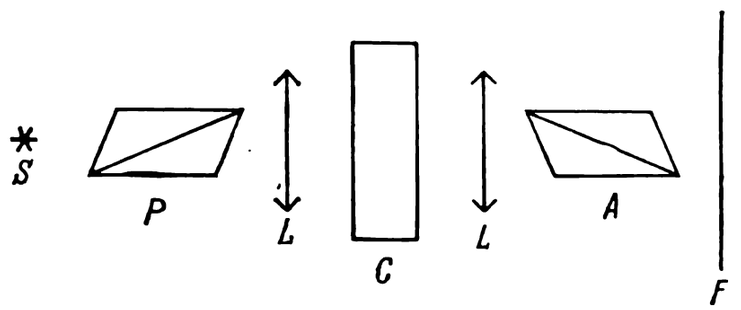


Fig. 40.3. Diagram of the observation of a crystal in convergent polarized light: L, L—condenser lenses, S—sources of light, P—polarizer, A—analyzer, C—crystal plate, F—screen

important role is played here by two condensers L. Moreover, the source of light is not a point one, as in Fig. 40.1, but a luminous plane which gives a wide beam of parallel rays*. Along the optic axis of the set-up there travels only one central beam, while the others are inclined toward the axis and pass through the studied crystal plate at different angles; the further the beam is from the centre of the field of vision, the larger are the angles.

Onto the examined crystal plate there falls a converging beam of polarized rays each of which is divided in the crystal into two rays with mutually perpendicular vibration planes. A second condenser lens gathers these rays and focuses them on the focal plane of a lens. Each beam of parallel rays that passed through the plate in some definite direction will converge in a single point in the focal plane of the lens. Observing this point through the analyzer one can see the result of the interference of the given beam of parallel rays. On the whole there can be seen in the field of vision the entire picture, which in a parallel beam could be seen consecutively by rotating the plate about the horizontal and vertical axes. As a result of the interference of the beams of light, passing through the crystal plate at all possible angles, characteristic interference pictures appear which are called *conoscopic pictures*. The appearance of a conoscopic picture depends on the symmetry of the crystal (on the crystallographic category), on the orientation of the optical indicatrix, on the thickness of the crystal and on the magnitude of its birefringence, as well as on the aperture of the microscope and the spectral composition of light.

The conoscopic pictures observed in crossed nicols consist of isogyres and isochromes. *Isogyres* are the dark bands, all points of which correspond to those directions in the crystal along which there propagate rays with the vibrations

* A conoscopic picture developing in the focal plane of the lens of a polarizing microscope can be seen with the naked eye upon removal of the eyepiece and the upper condenser.

parallel to the polarization planes of the crossed nicols. *Isochromes* are the coloured bands of various interference colours (at observation in white light), each of which corresponds to the directions of the same path-length difference.

If a crystal plate is rotated about the direction of a ray, the isogyres generally change their form and orientation, while the isochromes do not.

A characteristic conoscopic picture of a uniaxial crystal, cut out perpendicularly to its optic axis, appears as a black cross of two isogyres and a series of concentric coloured isochrome rings (in Fig. 40.4 the isochromes are shown as black and white bands). A complete revolution of the plate does not change the picture.

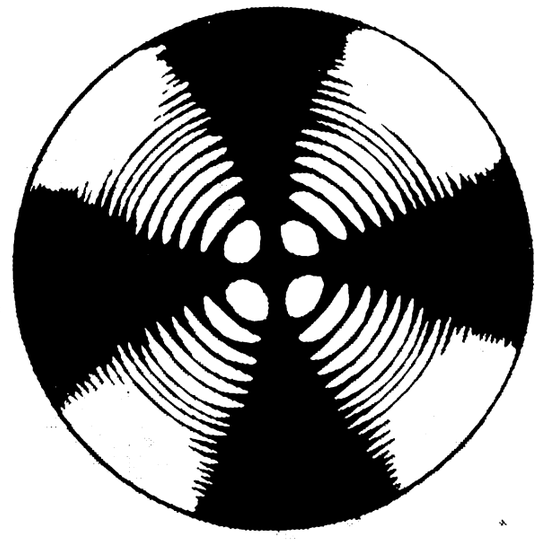


Fig. 40.4. Conoscopic picture of an optically uniaxial crystal observed perpendicularly to the optic axis

If a normal to the plate diverges from the optic axis of the crystal, the centre of the isogyre cross does not coincide with the centre of the field of vision, and during the rotation of the plate the cross describes a circle about the centre of the field of vision. If the angle between the optic axis of the plate and the ray is sufficiently large, only one isogyre will be seen in the field of vision, while in some positions the isogyres do not appear in the field of vision of the microscope at all (Fig. 40.5).

The conoscopic picture of a biaxial crystal in a section perpendicular to bisectrix of the acute angle, at a diagonal position of the plate, consists of two

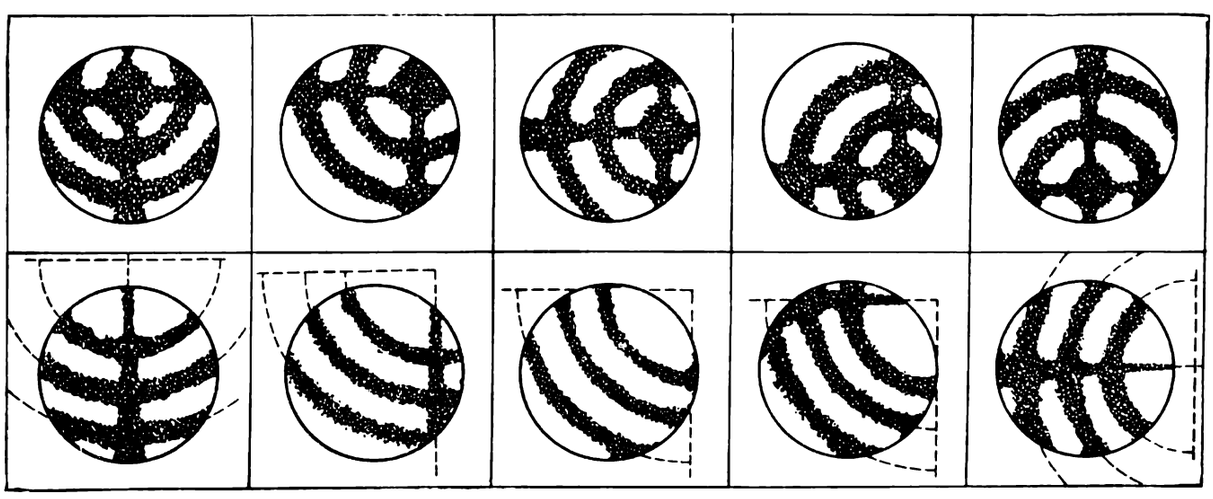


Fig. 40.5. Conoscopic picture of an optically uniaxial crystal observed at different angles to the optic axis

isogyres and a series of isochromes (Fig. 40.6). In section the isochromes have the shape of Cassini ovals, a special case of which is a lemniscate. The isogyres have the shape of hyperbolas (Fig. 40.6). Two points surrounded by the rings of lemniscates correspond to the exits of optic axes. Near the exits of the axes the lemniscates are arranged in concentric rings around each of the axes, and further on they form figures of eight common for both axes. The angle of optic axes of

a biaxial crystal $2V$ can be measured in a conoscopic picture by the distance between the exits of optic axes; when calculating this angle it is necessary to take into account the difference between the angles in the crystal and in air.

The surface of an equal phase difference is constructed for a biaxial crystal in the same way as for a uniaxial one.

The optical properties of crystals, in particular, tensors $\varkappa$ and η, the refractive index n, depend on the frequency of light, temperature and other factors. The corresponding phenomenon is called *dispersion* (frequency dispersion, temperature dispersion, etc.; in Sec. 81 space dispersion will be discussed). Most essential is the frequency dispersion. The character of the dispersion of optical tensors in crystals of different symmetries differs essentially. Thus, in optically

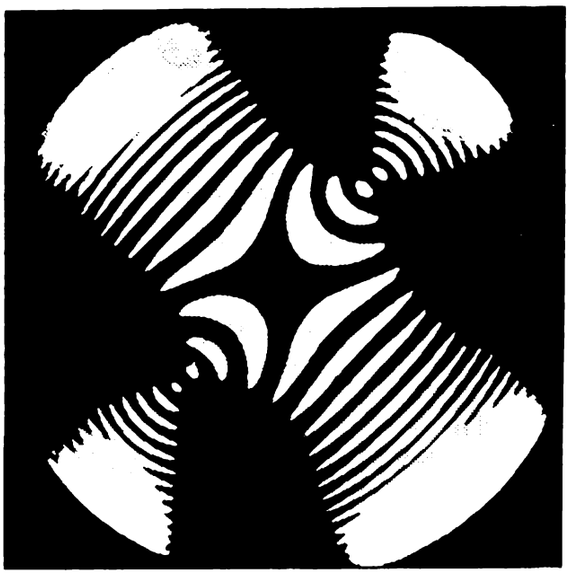


Fig. 40.6. Conoscopic picture of a biaxial crystal observed perpendicularly to the bisectrix of the acute angle.

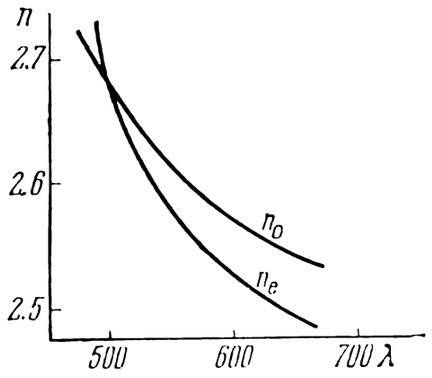


Fig. 40.7. Dispersion of the refractive indices of thiogallate of silver (Hobden, 1968)

isotropic crystals it comes to the dispersion of the refractive index: $n = n(\omega)$. In optically uniaxial crystals both principal refractive indices depend on frequency: $N_o = N_o(\omega)$, $N_e = N_e(\omega)$. Although at frequencies for which the crystal is transparent the refractive indices always increase with frequency ($dN_o/d\omega > 0$ and $dN_e/d\omega > 0$), the rate of the increase can be so different that at a certain frequency the sign of birefringence will change. The crystal appears to be optically isotropic for the light of this frequency. Thus the tetragonal crystals of apophillite and torbernite are optically positive in red light, optically negative in blue light, and isotropic in green light. In a tetragonal crystal of vesuvian the change of sign is reversed: it is optically positive in blue light and negative in red light. A crystal of thiogallate of silver, $AgGaS_2$, is optically positive for light with a wavelength (in vacuum) less than 497.4 nm and optically negative for light with a greater wavelength. For light with $\lambda_0 = 497.4$ nm the crystal of silver thiogallate behaves, in spite of its tetragonal symmetry, as an optically isotropic medium (Fig. 40.7). The application of this peculiar phenomena is described in Sec. 81.

In optically uniaxial crystals the dispersion of both the refractive indices and birefringence is observed. The direction of the optic axis in these crystals is unambiguously determined by the crystal symmetry (it always coincides with the principal symmetry axis) and is therefore not subject to dispersion.

In optically biaxial crystals dispersion is highly varied, differing somewhat in the crystals of the different systems of the lower category.

In crystals of the rhombic system dispersion is possible of the principal refractive indices: $N_1 = N_1(\omega)$, $N_2 = N_2(\omega)$, $N_3 = N_3(\omega)$, while the direction of the principal axes of optical tensors $\varkappa(\omega)$ and $\eta(\omega)$ are rigidly tied up with the symmetry elements of crystals (2-fold axes or normals to symmetry planes) and are therefore not subject to dispersion. However, the directions of optic axes in crystals of the rhombic system, generally speaking, experience dispersion: with a change of frequency the optic axes turn toward each other or away from each other, remaining all the while in the symmetry plane of the optical tensors, and so that the bisectrices of the angles between optic axes retain their direction. The changes can be very great. For instance, in Rb_2SO_4 angle $2V$ for red light is 36°25′, and for blue light it is 61°50′. With a change of frequency the angle between optic axes may change from acute to obtuse or vice versa; at the frequency which corresponds to a right angle the optic sign of a biaxial

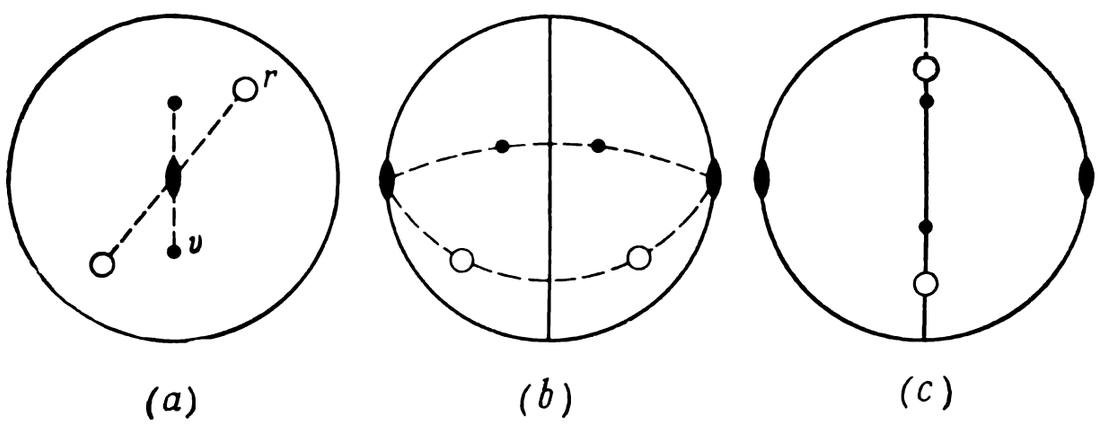


Fig. 40.8. Principal types of the dispersion of optic axes and bisectrices in monoclinic crystals: (a) crossed dispersion, (b) parallel dispersion, (c) inclined dispersion. Black dots denote emergence of axes for violet light (v), white dots, for red light (r)

crystal is reversed. Especially interesting is the case when in the course of a change of frequency one of the principal refractive indices becomes equal to the other one. For the light of this frequency the crystal is optically uniaxial: positive if at this frequency $N_m = N_p$, negative if $N_m = N_g$. However, the peculiarity of the situation does not end at this. The point is that as a rule the graphs $N_i = N_i(\omega)$ intersect at this frequency (their contact is much less probable), and therefore from different sides of the point of intersection, different (i.e. corresponding to different principal axes) principal refractive indices serve as the mean refractive indices N_m. And this, in its turn, means that for light of certain frequencies one symmetry plane of a crystal serves as the plane of optic axes, while for light of other frequencies another symmetry plane does.

In a brookite crystal (a rhombic modification of TiO_2) in red and yellow light the plane of optic axes is (001), and in blue light it is (010). For light with $\lambda = 670$ nm angle $2V$ of the optic axes of brookite is 58°, for $\lambda = 535$ nm, $2V$ is 21°40′, and for $\lambda = 550$ nm, angle $2V$ is 0, the crystal appears as optically uniaxial.

The dispersion of the refractive indices is seen directly in the conoscopic picture: dark edges of the hyperbolas near the exit of the optic axis acquire, as it were, a coloured border, with supplementary hues on the convex and concave sides of the hyperbola.

In crystals of the monoclinic system there is, besides the dispersion of the principal refractive indices the dispersion of the principal axes of optical tensors $\varkappa$ and η; since two principal axes of the three are the bisectrices of the angles between the optic axes, this dispersion is also called the *dispersion of bisectrices*. In crystals of the monoclinic system one principal axis of the three retains its direction (in the usual choice of the crystallographic system of coordinates this is the [010] direction), while the two other axes rotate about it remaining in the plane (010) perpendicular to it. The plane of the optic axes of a monoclinic system either coincides with the crystallographic plane (010) or is perpendicular to it; in the latter case, generally speaking, it rotates with respect to the crystal with the change of the frequency of light. Correspondingly, in monoclinic crystals two principal types of the dispersion of optic axes, shown schematically in Fig. 40.8, are possible.

In a conoscopic picture the dispersion of optic axes is seen not only as a coloured border of the isogyres but also as a change in the colouring of lemniscates; different colouring is observed on the one and on the other sides from the optic axis within the limits of the same ring.

Temperature dispersion is marked in the monoclinic crystal of gypsum ($CaSO_4 \cdot 7H_2O$). At room temperature the plane of optic axes is perpendicular to plane (010) and angle $2V$ between the optic axes is 62°. On heating the angle decreases so rapidly that at 116°C it is already zero, so that the crystal becomes optically uniaxial. On further heating the optic axes diverge again, but now in the (010) plane.

The character of the dispersion of optic axes is usually examined by observing a conoscopic picture in a section approximately perpendicular to the acute bisectrix. The dispersion changes of the conoscopic picture, with the plane of optic axes perpendicular to (010), differ somewhat in cases when the bisectrix of the acute angle coincides with [010] and when it is perpendicular to this direction: in the first case it is called *crossed* dispersion, in the second case, *horizontal* or *parallel dispersion*. When the angle between optic axes is close to 90°, these differences disappear.

On optical properties of crystals see Born (1965); Born, Wolf (1964); Born, Huang (1966); Ditchburn (1963); Karandeev (1913); Landau and Lifshits (1957); Landsberg (1957); Melankholin (1970); F. I. Fedorov (1958); Shubnikov (1958); Pockels (1906); Ramachandran, Ramaseshnan (1961).

Chapter V

SYMMETRY OF HIGHER-RANK TENSORS

Sec. 41. Tensors and Pseudotensors of Higher Ranks

In crystal physics there are used, along with the second-rank tensors, also tensors of the third, fourth and still higher ranks. They are introduced in the same manner as the second-rank tensors. Let, for example, the components of vector $\boldsymbol{P}$ be linearly dependent on the components of a second-rank tensor $\boldsymbol{\sigma}$:

$$P_l = d_{lmn}\sigma_{mn}; \tag{41.1}$$

d_{lmn} are the coefficients of the linear dependence. However, vector $\boldsymbol{P}$ and tensor $\boldsymbol{\sigma}$ could also be referred to another, a "new" system of coordinates. If $\| c_{i'l} \|$ is the matrix of the transition from the "old" to the new system of coordinates, then the components of vector $\boldsymbol{P}$ in the new system of coordinates are as follows:

$$P_{i'} = c_{i'l}P_l = c_{i'l}d_{lmn}\sigma_{mn}. \tag{41.2}$$

Let us express the values of components σ_{mn} of tensor $\boldsymbol{\sigma}$ in the old system of coordinates in terms of their values $\sigma_{j'k'}$ in the new system:

$$\sigma_{mn} = c_{j'm}c_{k'n}\sigma_{j'k'}. \tag{41.3}$$

Substituting σ_{mn} in (41.2) we obtain

$$P_{i'} = c_{i'l}d_{lmn}c_{j'm}c_{k'n}\sigma_{j'k'}. \tag{41.4}$$

If in the old system of coordinates the linear dependence of the components of vector $\boldsymbol{P}$ on the components of tensor $\boldsymbol{\sigma}$ was defined by the set of coefficients d_{lmn}, the same relation in the new system is defined by coefficients

$$d_{i'k'} = c_{i'l}c_{j'm}c_{k'n}d_{lmn}. \tag{41.5}$$

In the same way we derive the formula for changing coefficients d_{lmn} under the transition to the old system from the new one:

$$d_{lmn} = c_{i'l}c_{j'm}c_{k'n}d_{i'j'k'}. \tag{41.6}$$

The transformation laws (41.5) and (41.6) are the same as for the products of the components of three vectors. Thus we have to deal with a certain geometric, i.e. existing independently of coordinate

systems, quantity **d** which in each system of coordinates is specified by a set of numbers d_{lmn}; in changing over from one system of coordinates to another one these numbers are transformed as the products of the components of three vectors. Such a quantity is called a *tensor of the third rank*, and numbers d_{lmn} and $d_{i'j'k'}$ are the *components* of this tensor in the old and in the new system of coordinates respectively.

A third-rank tensor can be attained by another method—by considering the linear dependence of the components of a second-rank tensor ζ on the components of vector $\boldsymbol{E}$:

$$\zeta_{ij} = r_{ijk}E_k; \tag{41.7}$$

coefficients r_{ijk} are also the components of a third-rank tensor **r**.

The same methods allow introducing the fourth-, fifth- and still higher-rank tensors. For instance, coefficients s_{ijkl} determining the linear dependence of components ε_{ij} of tensor ε on components σ_{kl} of tensor σ

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}, \tag{41.8}$$

are the components of a fourth-rank tensor **s**, coefficients Q_{ijklm} determining the linear dependence of s_{ijkl} components of a fourth-rank tensor **s** on the components E_m of vector $\boldsymbol{E}$

$$s_{ijkl} = Q_{ijklm}E_m, \tag{41.9}$$

are the components of a fifth-rank tensor **Q**. The following general rule can be formulated: the coefficients of a linear dependence of the components of an r-rank tensor on the products of the components of $r_1, \ldots, r_k$-rank tensors are themselves the components of a tensor of rank $r + r_1 + \ldots + r_k$.

Another process in the result of which tensors are formed is the differentiation of tensors with respect to tensors. Let, for instance, the components of vector $\boldsymbol{P}$ be functions of the components of tensor σ. We shall introduce the notation of partial derivatives

$$\frac{\partial P_l}{\partial \sigma_{mn}} = d_{lmn}, \tag{41.10}$$

and we shall denote the corresponding partial derivatives in the new system of coordinates as

$$\frac{\partial P_{i'}}{\partial \sigma_{j'k'}} = d_{i'j'k'}. \tag{41.11}$$

As can be easily shown*

$$d_{i'j'k'} = c_{i'l}c_{j'm}c_{k'n}d_{lmn}; \tag{41.12}$$

this meaning that d_{lmn} are the components of a third-rank tensor. The differentiation of a tensor with respect to several tensors is considered similarly. As a result we arrive at the following general rule: the partial derivatives of the components of an r-rank tensor with respect to the components of tensors of ranks $r_1, \ldots, r_k$ are themselves the components of a tensor whose rank is $r + r_1 + \ldots + r_k$.

Tensors of higher ranks can also be written in a non-coordinate form with the aid of basic vectors, e.g.

$$\mathbf{d} = d_{lmn}\boldsymbol{e}_l\boldsymbol{e}_m\boldsymbol{e}_n. \tag{41.13}$$

The transition to a new basis, i.e. the replacement of vectors $\boldsymbol{e}_l$ by their linear combinations $\boldsymbol{e}_{i'} = c_{i'l}\boldsymbol{e}_l$ (where vectors $\boldsymbol{e}_{i'}$ as well as vectors $\boldsymbol{e}_l$ are orthonormalized), as can be easily calculated, results in the same tensor appearing as

$$\mathbf{d} = d_{i'j'k'}\boldsymbol{e}_{i'}\boldsymbol{e}_{j'}\boldsymbol{e}_{k'}, \quad d_{i'j'k'} = c_{i'l}c_{j'm}c_{k'n}d_{lmn} \tag{41.14}$$

in full agreement with (41.5) and (41.12).

Let us go over to the rules for operations on tensors.

Multiplication by a number. The *product of tensor* **A** with components (referred to a certain already given orthonormalized basis $\boldsymbol{e}_1\boldsymbol{e}_2\boldsymbol{e}_3$) $A_{ij\ldots k}$ *by number* λ is a tensor of the same rank $\lambda\mathbf{A}$ with components (referred to the same basis) $\lambda A_{ij\ldots k}$.

Addition of Tensors. The *sum* of two tensors of the same rank, **A** and **B**, with components $A_{ij\ldots k}$ and $B_{ij\ldots k}$ respectively is a tensor of the same rank **D** with components $D_{ij\ldots k} = A_{ij\ldots k} + B_{ij\ldots k}$. Tensors of different ranks cannot be added together.

---

* We know that

$$P_{i'} = c_{i'l}P_l.$$

Since the elements of the transformation matrix do not depend on σ,

$$\frac{\partial P_{i'}}{\partial \sigma_{j'k'}} = c_{i'l}\frac{\partial P_l}{\partial \sigma_{j'k'}}.$$

On the other hand

$$\frac{\partial}{\partial \sigma_{j'k'}} = \frac{\partial \sigma_{mn}}{\partial \sigma_{j'k'}}\frac{\partial}{\partial \sigma_{mn}}.$$

Since $\sigma_{mn} = c_{j'm}c_{k'n}\sigma_{j'k'}$,

$$\frac{\partial \sigma_{mn}}{\partial \sigma_{j'k'}} = c_{j'm}c_{k'n}.$$

Therefore

$$\frac{\partial P_{i'}}{\partial \sigma_{j'k'}} = c_{i'l}c_{j'm}c_{k'n}\frac{\partial P_l}{\partial \sigma_{mn}},$$

this resulting in formula (41.12).

Multiplication of Tensors. The *product of tensor* **A** of rank p and components $A_{i_1 \ldots i_p}$ by tensor **B** of rank q and components $B_{k_1 \ldots k_q}$ is a tensor $\mathbf{D} = \mathbf{AB}$ of rank $p + q$ with components

$$D_{i_1 \ldots i_p k_1 \ldots k_q} = A_{i_1 \ldots i_p} B_{k_1 \ldots k_q}.$$

The sequence of the factors is essential: tensor $\mathbf{F} = \mathbf{BA}$, generally speaking, is not equal to tensor **D**. When applied to vectors, this multiplication is called *dyadic multiplication.*

Formation of Isomers. Permuting in some way the indices of tensor **D** we obtain tensor **F** of the same rank as **D**—one of the *isomers* of tensor **D**. In particular, in the above instance of multiplication of tensors tensor $\mathbf{F} = \mathbf{BA}$ is an isomer of tensor $\mathbf{D} = \mathbf{AB}$:

$$F_{k_1 \ldots k_q i_1 \ldots i_p} = D_{i_1 \ldots i_p k_1 \ldots k_q}.$$

Symmetrization and Alternation. Tensor **B** is a *symmetrized tensor* **A** if it is equal to the arithmetic mean of all the possible isomers of tensor **A**; tensor **D** is an *alternated tensor* **A**, if in the above mentioned arithmetic mean the isomers obtained by an even permutation of indices are taken with the plus sign, and by an odd permutation with a minus sign. Symmetrization and alternation are denoted by enclosing the indices into parentheses or brackets respectively. For example

$$B_{ijk} = A_{(ijk)} = \frac{1}{6}(A_{ijk} + A_{jki} + A_{kij} + A_{ikj} + A_{jik} + A_{kji}),$$

$$D_{ijk} = A_{[ijk]} = \frac{1}{6}(A_{ijk} + A_{jki} + A_{kij} - A_{ikj} - A_{jik} - A_{kji}).$$

Symmetrization and alternation may be done not for all the indices, but only for the part of them which is enclosed in brackets. For instance

$$A_{i(jk)} = \frac{1}{2}(A_{ijk} + A_{ikj}), \quad A_{[ij]k} = \frac{1}{2}(A_{ijk} - A_{jik}).$$

Contraction of Tensors. Tensor **B** of rank $r - 2$ can be obtained from tensor **A** of rank $r \geqslant 2$, if the summation of the latter's components is done with respect to some pair of indices. For example, tensor **B** with components $B_{ijk} = A_{ijkll}$ is the result of a *contraction* of a fifth-rank tensor with respect to the last two indices. At another choice of indices for contraction we obtain another third-rank tensor; for instance, $D_{ijk} = A_{llijk}$, $C_{ijk} = A_{lijlk}$; generally speaking, $D \neq B \neq C$. Contraction is often combined with multiplication. For example, formula $P_i = d_{ijk}\sigma_{jk}$ contains multiplication of tensor **d** by tensor $\boldsymbol{\sigma}$ and a subsequent twofold contraction of the obtained fifth-rank tensor.

In each of the above definitions it is the word "tensor" that calls for proof: it must be proved that a set of quantities resulting from the operations is transformed, according to the tensor law, under transition from one system of coordinates to another. In other words, it is necessary to verify that the following two ways lead to the same results: (1) we perform a corresponding operation (addition, multiplication, contraction, etc.) on tensor components in the old system of coordinates, then, believing that the obtained quantities are tensor components, we refer them to the new system of coordinates; (2) we refer the components of all given tensors to the new system of coordinates and only thereupon perform the corresponding operation on them.

Let us consider, for example, the multiplication of a first-rank tensor **A** by a second-rank tensor **B**:

1st way: $A_l B_{mn} = D_{lmn}$, $D^{(1)}_{i'j'k'} = c_{i'l} c_{j'm} c_{k'n} D_{lmn}$;

2nd way: $A_{i'} = c_{i'l} A_l$, $B_{j'k'} = c_{j'm} c_{k'n} B_{mn}$, $D^{(2)}_{i'j'k'} = A_{i'} B_{j'k'}$;

it must be proved that $D^{(1)}_{i'j'k'} = D^{(2)}_{i'j'k'}$.

Along with tensors *pseudotensors* are also used in crystal physics. Tensor **A** of rank r is a set of 3^r quantities $A_{k_1 \ldots k_r}$, transforming under transition from the old coordinates to the new ones according to the law

$$A_{i'_1 \ldots i'_r} = c_{i'_1 k_1} \ldots c_{i'_r k_r} A_{k_1 \ldots k_r}, \tag{41.15}$$

where $\| c_{i'k} \|$ is the transformation matrix. A pseudotensor **B** differs from tensor **A** of the same rank under transition to the new coordinates in that its components $B_{k_1 \ldots k_r}$ are additionally multiplied by the determinant of the transformation matrix $\Delta = \det \| c_{i'k} \|$:

$$B_{i'_1 \ldots i'_r} = \Delta c_{i'_1 k_1} \ldots c_{i'_r k_r} B_{k_1 \ldots k_r}. \tag{41.16}$$

Pseudotensors of lower ranks—a pseudoscalar and a pseudovector—were discussed in Sec. 23. A zero-rank pseudotensor, or a pseudoscalar, is a one-component quantity ψ transforming according to the law $\psi' = \Delta\psi$; a first-rank pseudotensor, or a pseudovector, is an axial vector $\mathring{\boldsymbol{a}}$ whose components a_k transform in accordance with formula $a_{i'} = \Delta c_{i'k} a_k$.

Sec. 42. Internal Symmetry of Tensors and Duality Relations

In crystal physics there are often used higher-rank tensors symmetric with respect to some indices. A tensor is called *symmetric* with respect to two or several indices if all its isomers differing one from another by permutations of these indices are all equal among themselves. Thus, the components of a third-rank tensor symmetric with respect to the last two indices, satisfy conditions

$$d_{ikl} = d_{ilk}, \tag{42.1}$$

the components of a third-rank tensor symmetric with respect to all the three indices satisfy conditions

$$f_{ikl} = f_{ilk} = f_{kli} = f_{kil} = f_{lik} = f_{lki}, \tag{42.2}$$

and the components of a fourth-rank tensor symmetric with respect to the first two and the last two indices satisfy conditions

$$p_{ijkl} = p_{jikl} = p_{ijlk} = p_{jilk}. \tag{42.3}$$

In crystal physics there also occur tensors which are symmetric with respect to whole groups of indices. Such is, for instance, a fourth-rank tensor in which indices can be permuted in the first and the second pair, and, also the pairs themselves can be permuted:

$$s_{ijkl} = s_{jikl} = s_{ijlk} = s_{jilk} = s_{klij} = s_{klji} = s_{lkij} = s_{lkji}. \tag{42.4}$$

A second example of this kind is provided by a tensor in which only pairs of indices can be permuted, but not the indices within the pairs:

$$n_{ijkl} = n_{klij}. \tag{42.5}$$

The ability of a tensor to be symmetric or antisymmetric with respect to some indices or groups of indices is called the *internal symmetry* of the tensor. But it still has to be proved that the internal symmetry is actually the property of the tensor. The proofs are very simple; in essence they reduce to the following: if we find some kind of internal symmetry upon referring a tensor to a certain system of coordinates, we shall find the same kind of internal symmetry in any other system of coordinates.

A theorist-physicist, Jahn (1949), suggested a simple and convenient system of notation for avoiding clumsily worded descriptions of the internal symmetry of tensors. The internal symmetry of a vector is denoted by the letter V. The internal symmetry of an r-rank tensor is denoted by the symbol V^r reminding that the components of an r-rank tensor are transformed as the products of the components of r vectors.

A symmetric second-rank tensor is denoted $[V^2]$, this symbol showing that the components of the given tensor are transformed as the products of two components of one and the same vector. In general, the internal symmetry of an r-rank tensor symmetric with respect to all indices is denoted by $[V^r]$: this meaning that its components are transformed as the products of the r components of one and the same vector. Thus, the internal symmetry of tensor **f** characterized by (42.2) is denoted by $[V^3]$. If an r-rank tensor is symmetric with respect to q indices, its internal symmetry is denoted by

$[V^q]\ V^{r-q}$; for example, the internal symmetry characterized by (42.1) is denoted by $V\ [V^2]$*.

There is also more complicated notation.

$[V^2]\ [V]^2$ or simply $[V^2]^2$ is the internal symmetry of a fourth-rank tensor symmetric with respect to the first and second pairs of indices (42.3);

$[V^2]^3$ is the internal symmetry of a sixth-rank tensor symmetric with respect to the first, second and third pairs of indices;

$[(V^2)^2]$ is the internal symmetry of a fourth-rank tensor symmetric with respect to the permutation of pairs of indices (42.5);

$[[V^2]^2]$ is the internal symmetry of a fourth-rank tensor symmetric with respect to the first and second pairs of indices and also with respect to their permutation (42.4).

In all cases the total power of V is equal to the rank of the tensor.

Jahn's symbols permit describing the internal symmetry of pseudotensors too. The prefix "pseudo" is denoted by ε: the internal symmetry of a pseudovector (i.e. an axial vector, see Sec. 23) is expressed by symbol εV, of a symmetric second-rank pseudotensor, by symbol $\varepsilon\ [V^2]$ and so on. The internal symmetry of a scalar is denoted by symbol 1, then the internal symmetry of a pseudoscalar is naturally denoted by ε.

In crystal physics symmetric higher-rank tensors often define linear dependences in which symmetric second-rank tensors participate. For example, a tensor of internal symmetry $V\ [V^2]$ (see (42.1)) defines the linear dependence of a symmetric second-rank tensor $[V^2]$ on vector V:

$$\varepsilon_{kl} = d_{ikl}E_i \quad (\varepsilon_{kl} = \varepsilon_{lk}), \tag{42.6}$$

while tensor $[V^2]^2$ (see (42.3)) defines the linear dependence of one symmetric second-rank tensor $[V^2]$ on another one

$$\zeta_{ij} = p_{ijkl}\varepsilon_{kl}\ (\zeta_{ij} = \zeta_{ji},\ \varepsilon_{kl} = \varepsilon_{lk}). \tag{42.7}$$

Symmetric higher-rank tensors are also obtained as a result of differentiation with respect to tensor arguments. Thus, the differentiation of a scalar function with respect to vector V and a symmetric second-rank tensor $[V^2]$ results in tensor $V\ [V^2]$ (see (42.1):

$$d_{ikl} = -\frac{\partial^2\Phi}{\partial E_i \partial\sigma_{kl}} \quad (\sigma_{kl} = \sigma_{lk}); \tag{42.8}$$

and twofold differentiation of a scalar function with respect to the components of a symmetric second-rank tensor $[V^2]$ results in a tensor

* The notation of internal symmetry does not indicate the places of indices with respect to which the tensor is symmetric; it relates to all isomers, but in verbal descriptions and examples the one most convenient or more often used in crystal physics is chosen.

of internal symmetry $[[V^2]^2]$ (see (42.4)):

$$s_{ijkl} = -\frac{\partial^2 \Phi}{\partial \sigma_{ij} \partial \sigma_{kl}} \quad (\sigma_{ij} = \sigma_{ji}), \tag{42.9}$$

while a twofold differentiation with respect to a non-symmetric second-rank tensor V^2 produces a tensor $[(V^2)^2]$ (see (42.5)):

$$n_{ijkl} = -\frac{\partial^2 \Phi}{\partial \gamma_{ij} \partial \gamma_{kl}} \quad (\gamma_{ij} \neq \gamma_{ji}). \tag{42.10}$$

Symmetric tensors have a smaller number of independent components than non-symmetric ones. While tensor V^3 has 27 (3^3) independent components, tensor $V\ [V^2]$ has only 18 (6×3) of them (this is especially evident from (42.6) and (42.8)), and tensor $[V^3]$ has only 10 (3 components of the kind f_{111} + 6 components of the kind f_{122} + 1 component of the kind f_{123}). Similarly, tensor V^4 has 81 (3^4) independent components, tensor $[V^2]^2$ has 36 (6^2) of them, tensor of the $[[V^2]^2]$ kind has 21 $[6 \times (6 + 1)/2]$, and tensor of the $[(V^2)^2]$ kind has 45 $[9 \times (9 + 1)/2]$ independent components.

Along with symmetric tensors there are also used the antisymmetric ones*. A tensor is called *antisymmetric* with respect to two or three indices**, if its isomers, differing from each other by an even permutation of these indices, are equal between themselves, and differing by an odd permutation are "antiequal" (equal in magnitude but opposite in sign). According to Jahn, the antisymmetry of tensors is denoted similarly to symmetry, but in braces instead of in the square brackets. For example, the internal symmetry of a third-rank tensor antisymmetric with respect to the first two indices is denoted by $V\ \{V^2\}$ or $\{V^2\}\ V$ and is characterized by the equalities

$$\beta_{ijk} = -\beta_{jik}, \tag{42.11}$$

and the internal symmetry of a third-rank tensor antisymmetric with respect to all indices is denoted by $\{V^3\}$ and is characterized by equalities***

$$e_{ijk} = e_{jki} = e_{kij} = -e_{ikj} = -e_{jik} = -e_{kji}. \tag{42.12}$$

This tensor is remarkable in that it has only one independent component. Indeed, if among the indices there are at least two equal ones, the corresponding component is zero, and all the six components that differ from zero have as their indices some permutation of the numbers 1, 2, 3 and are therefore interconnected by five

* Sometimes the term "skew-symmetric" is used instead of "antisymmetric".

** In a three-dimensional space the tensors that are antisymmetric with respect to more than three indices are identically equal to zero.

*** Jahn's symbols are based on the notation for representations according to which the corresponding tensors are transformed, so V^2, $[V^r]$ and $\{V^r\}$ are the simple, symmetric and antisymmetric powers of the vector representation V.

equalities (42.12). If, for example, $e_{123} = 1$, then

$$e_{lmn} = \begin{cases} 1 & \text{for} \quad lmn = 123,\ 231,\ 312; \\ -1 & \text{for} \quad lmn = 132,\ 213,\ 321; \\ 0 & \text{in all other cases.} \end{cases} \tag{42.13}$$

The behaviour of the components of tensor **e** under a coordinate transformation is curious. If in the old system of coordinates these components are defined by (42.13), in the new system, the transition to which is specified by matrix $\| c_{i'l} \|$, they are $e_{i'j'k'} = c_{i'l} \times \times c_{j'm} c_{k'n} e_{lmn}$. Upon the calculation of this sum for several values of $i'j'k'$ and the comparison of it with the quantity $\Delta = \det \| c_{i'l} \|$, we shall become convinced that

$$e_{i'j'k'} = \begin{cases} \Delta & \text{for} \quad i'j'k' = 123,\ 231,\ 312; \\ -\Delta & \text{for} \quad i'j'k' = 132,\ 213,\ 321; \\ 0 & \text{in all other cases.} \end{cases} \tag{42.14}$$

On the other hand, a comparison of (42.13) and (42.14) shows that under a change to a new system of coordinates all the components of tensor **e** (or, if you will, its only independent component) are multiplied by the determinant of the transformation matrix, i.e. they are pseudoscalars (cf. (42.11)). Thus, this tensor is invariant with respect to all of its possible proper rotations, i.e. with respect to the group of rotations its symmetry is $\infty\infty$.

The Levi-Civita symbol was defined in Sec. 13 by the condition

$$\sigma_{lmn} = \begin{cases} 1 & \text{for} \quad lmn = 123,\ 231,\ 312; \\ -1 & \text{for} \quad lmn = 132,\ 213,\ 321; \\ 0 & \text{in all other cases} \end{cases} \tag{42.15}$$

in any system of coordinates. A comparison with tensor **e** shows that to be invariant (see above) tensor $\boldsymbol{\delta}$ should be a third-rank pseudotensor, so that under transition to a new system of coordinates its components transform according to the law

$$\delta_{i'j'k'} = \Delta c_{i'l} c_{j'm} c_{k'n} \delta_{lmn}, \tag{42.16}$$

where $\Delta = \det \| c_{i'l} \|$. Since these components do not change under any orthogonal transformations whatever, the symmetry group of tensor $\boldsymbol{\delta}$ is an orthogonal group $\infty\infty m$.

With the aid of the Levi-Civita pseudotensor the connection between a pseudoscalar and an antisymmetric third-rank tensor can be represented analytically:

$$e_{ijk} = \psi \delta_{ijk}, \quad \psi = \frac{1}{6} \delta_{ijk} e_{ijk}; \tag{42.17}$$

here ψ is a unit pseudoscalar equal to -1 in a right-hand system of coordinates and to -1 in a left-hand one.

The Levi-Civita pseudotensor also allows to ascertain a two-way correspondence between the axial vector $\mathring{\boldsymbol{a}}$ and the antisymmetric second-rank tensor $\mathbf{A} = -\mathbf{A}^*$:

$$A_{mn} = -\delta_{lmn} a_l, \quad a_l = -\frac{1}{2}\delta_{lmn} A_{mn}. \tag{42.18}$$

This correspondence persists no matter what orthogonal transformations are performed. In fact,

$$-\delta_{i'j'k'} a_{i'} = -\Delta c_{i'l} c_{j'm} c_{k'n} \delta_{lmn} \Delta c_{i'p} a_p =$$

$$= -c_{j'm} c_{k'n} \delta_{lmn} \delta_{lp} a_p = -c_{j'm} c_{k'n} \delta_{lmn} a_l = c_{j'm} c_{k'n} A_{mn} = A_{j'k}$$

(use was made here of (42.16), identities $\Delta^2 = 1$ and $c_{i\ l} c_{i'p} = \delta_{lp}$).

In fact, the axial vector $\mathring{\boldsymbol{a}}$ and the antisymmetric tensor $\mathbf{A}$ connected by relations (42.18) are two forms of denoting one and the same geometric object. The same can be said, of course, about the tensor $\mathbf{e}$ of internal symmetry $\{V^3\}$ and the pseudoscalar ψ which are connected with each other by relations (42.17).

Relations (42.17), (42.18) and others similar to them are called the *relations of duality*: an antisymmetric second-rank tensor is dual of an axial vector, an antisymmetric third-rank tensor, of a pseudoscalar, while an antisymmetric third-rank pseudotensor of a scalar.

Relations of duality can be very briefly and expressively written in Jahn's symbols: relation (42.17) as

$$\{V^3\} \sim \varepsilon, \tag{42.19}$$

and relation (42.18) as

$$\{V^2\} \sim \varepsilon V. \tag{42.20}$$

The principal advantage of this form of notation is the possibility of purely formal derivation of new duality relations from those already known. Thus, multiplying both parts of relation (42.19) by ε and noting that $\varepsilon^2 = 1$ (the product of two pseudoscalars is a scalar) we obtain

$$\varepsilon \{V^3\} \sim 1 \tag{42.21}$$

which is the relation of duality between an antisymmetric pseudotensor of the third rank and a scalar. Multiplying both sides of (42.20) by V, we obtain

$$\{V^2\} V \sim \varepsilon V^2 \tag{42.22}$$

which shows that a third-rank tensor, antisymmetric with respect to two indices, is dual of a second-rank pseudotensor which is, generally speaking, non-symmetric. Multiplying both sides of (42.20) by ε we find

$$\varepsilon \{V^2\} \sim V \tag{42.23}$$

which means that an antisymmetric second-rank pseudotensor is dual of an ordinary polar vector. Relations (42.22) and (42.23) are used in the theory of the optical activity of crystal (see Sec. 81).

Sec. 43. Non-Coordinate Notation of Tensors. Invariant Differential Operations on Tensors

As has already been mentioned in Sec. 41, higher-rank tensors can be denoted in a non-coordinate form. For example, a third-rank tensor in non-coordinate notation appears as $\mathbf{d} = d_{ijk}\mathbf{e}_i\mathbf{e}_j\mathbf{e}_k$. The non-coordinate notation of the multiplication of a tensor by a number and of the addition of tensors calls for no explanations. For the multiplication of tensors we write out the multiplied tensors in a row in due order without any signs between them. The multiplication with consequent contraction is naturally denoted by the sign of a *scalar product*. Indeed, if we agree that the sign of a scalar product means scalar multiplication of the adjacent vectors, then, for example, the scalar product of the vector $\boldsymbol{P} = P_l\boldsymbol{e}_l$ by the tensor $\mathbf{d}$ is

$$\boldsymbol{P}\cdot\mathbf{d} = P_l\boldsymbol{e}_l\cdot d_{ijk}\boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_k = P_l d_{ijk}\,(\boldsymbol{e}_l\cdot\boldsymbol{e}_i)\,\boldsymbol{e}_j\boldsymbol{e}_k = \\ = P_l d_{ijk}\delta_{li}\boldsymbol{e}_j\boldsymbol{e}_k = P_i d_{ijk}\boldsymbol{e}_j\boldsymbol{e}_k. \qquad (43.1)$$

The result is a second-rank tensor with components $P_i d_{ijk}$.

If the summation were done with respect to the last indices of tensor $\mathbf{d}$ a corresponding tensor could be obtained by the permutation of the factors:

$$\mathbf{d}\cdot\boldsymbol{P} = d_{ijk}\boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_k\cdot P_l\boldsymbol{e}_l = d_{ijk}P_k\boldsymbol{e}_i\boldsymbol{e}_j. \qquad (43.2)$$

But if the summation were to be done with respect to the middle index of tensor $\mathbf{d}$ we would not be able to write this operation in a non-coordinate form at all. Fortunately such contingencies are usually avoided in the notation of tensor relations in crystal physics. The saving remedy is the internal symmetry of tensors which are used in crystal physics. Indeed, if tensor $\mathbf{d}$ were symmetric with respect to all indices, it would not have mattered which of them was chosen for the summation index. Even if tensor $\mathbf{d}$ is symmetric only with respect to two indices (say, the second and third ones), this will suffice for denoting in a non-coordinate form all the possible contractions of this tensor with its vector, because in this case the summation with respect to the second index will give the same result as the summation with respect to the third index.

The natural generalization of the above scalar product of two tensors (i.e. of their multiplication with subsequent contraction with respect to one index of each tensor) is the *biscalar product* of tensors which differs from the scalar one in that the contraction is performed with respect to two indices of each tensor. The symbol of biscalar multiplication (:) shows that the two vectors directly to the left of it are scalarly multiplied by two vectors directly to the right of it. If, for instance, $\mathbf{s} = s_{ijkl}\boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_k\boldsymbol{e}_l$ and $\boldsymbol{\sigma} = \sigma_{mn}\boldsymbol{e}_m\boldsymbol{e}_n$,

then the biscalar product of these tensors is a second-rank tensor

$$\boldsymbol{\varepsilon} = \mathbf{s} : \boldsymbol{\sigma} = s_{ijkl}\boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_k\boldsymbol{e}_l : \sigma_{mn}\boldsymbol{e}_m\boldsymbol{e}_n =$$
$$= s_{ijkl}\sigma_{mn}\boldsymbol{e}_i\boldsymbol{e}_j(\boldsymbol{e}_k\cdot\boldsymbol{e}_m)(\boldsymbol{e}_l\cdot\boldsymbol{e}_n) = s_{ijkl}\sigma_{kl}\boldsymbol{e}_i\boldsymbol{e}_j. \quad (43.3)$$

The components ε_{ij} of the biscalar product $\mathbf{s} : \boldsymbol{\sigma}$ are equal, thus $\varepsilon_{ij} = s_{ijkl}\sigma_{kl}$. A biscalar product $\boldsymbol{\eta} = \boldsymbol{\sigma} : \mathbf{s}$ apparently has components $\eta_{kl} = \sigma_{ij}s_{ijkl}$.

The components of third- and fourth-rank tensors can be denoted with the aid of the symbol of a biscalar product. For example, the components of a third-rank tensor $\mathbf{d}$ and a fourth-rank tensor $\mathbf{s}$ are respectively equal as follows:

$$d_{ikl} = \boldsymbol{e}_i\cdot\mathbf{d} : \boldsymbol{e}_k\boldsymbol{e}_l,$$
$$s_{ijkl} = \boldsymbol{e}_i\boldsymbol{e}_j : \mathbf{s} : \boldsymbol{e}_k\boldsymbol{e}_l. \quad (43.4)$$

The biscalar multiplication can be applied to second-rank tensors too. For instance, the components of a second-rank tensor $\boldsymbol{\sigma}$ can be written out in any of the three equivalent forms:

$$\sigma_{ij} = \boldsymbol{e}_i\cdot\boldsymbol{\sigma}\cdot\boldsymbol{e}_j = \boldsymbol{\sigma} : \boldsymbol{e}_i\boldsymbol{e}_j = \boldsymbol{e}_i\boldsymbol{e}_j : \boldsymbol{\sigma}. \quad (43.5)$$

In non-coordinate notation the symbol $\times$ is also used, meaning the vector multiplication of the vectors adjacent to it. For example, the vector product of tensor $\boldsymbol{\sigma} = \sigma_{ij}\boldsymbol{e}_i\boldsymbol{e}_j$ by vector $\boldsymbol{p} = p_k\boldsymbol{e}_k$ is equal, by definition, to

$$\boldsymbol{\sigma} \times \boldsymbol{p} = \sigma_{ij}\boldsymbol{e}_i\boldsymbol{e}_j \times p_k\boldsymbol{e}_k = \sigma_{ij}p_k\boldsymbol{e}_i(\boldsymbol{e}_j \times \boldsymbol{e}_k),$$

and with the aid of identity $\boldsymbol{e}_j \times \boldsymbol{e}_k = \delta_{jkl}\boldsymbol{e}_l$ it is finally

$$\boldsymbol{\sigma} \times \boldsymbol{p} = \delta_{jkl}\sigma_{ij}p_k\boldsymbol{e}_i\boldsymbol{e}_l. \quad (43.6)$$

In the physics of continuous media invariant differential operations are extensively used: gradient of a scalar field $\varphi(\boldsymbol{r})$ (denoted grad φ) as well as divergence (div $\boldsymbol{u}$) and curl (curl $\boldsymbol{u}$) of a vector field $\boldsymbol{u}(\boldsymbol{r})$. Similar operations can be performed on quantities of higher tensor ranks. We shall use the same notations in such cases, but with capital first letters.

The gradient of the vector field $\boldsymbol{u}(\boldsymbol{r})$ is a second-rank tensor Grad $\boldsymbol{u}$ with components

$$(\mathrm{Grad}\,\boldsymbol{u})_{ij} = \frac{\partial u_j}{\partial x_i}. \quad (43.7)$$

Tensor $\partial\boldsymbol{u}/\partial\boldsymbol{r}$ transposed of it is called the *derivative of vector field* $\boldsymbol{u}$ *with respect to radius-vector* $\boldsymbol{r}$:

$$\left(\frac{\partial\boldsymbol{u}}{\partial\boldsymbol{r}}\right)_{ij} = \frac{\partial u_i}{\partial x_j}. \quad (43.8)$$

The symmetric part of each of the tensors is called the *deformation of the vector field* $\boldsymbol{u}(\boldsymbol{r})$ and is denoted Def $\boldsymbol{u}$:

$$\mathrm{Def}\,\boldsymbol{u}=\frac{1}{2}\left(\mathrm{Grad}\,\boldsymbol{u}+\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{r}}\right),\qquad (\mathrm{Def}\,\boldsymbol{u})_{ij}=\frac{1}{2}\left(\frac{\partial u_i}{\partial x_i}+\frac{\partial u_j}{\partial x_i}\right). \tag{43.9}$$

The divergence of the tensor field $\boldsymbol{\sigma}(\boldsymbol{r})$ is vector Div $\boldsymbol{\sigma}$ with components

$$(\mathrm{Div}\,\boldsymbol{\sigma})_j=\frac{\partial \sigma_{ij}}{\partial x_i}. \tag{43.10}$$

When differentiation is to be done with respect to the second index, the divergence of the transposed tensor $\boldsymbol{\sigma}^*$ is used:

$$(\mathrm{Div}\,\boldsymbol{\sigma}^*)_j=\frac{\partial \sigma_{jk}}{\partial x_k}. \tag{43.11}$$

If the tensor field $\boldsymbol{\sigma}(\boldsymbol{r})$ is determined at all points of surface S, the surface integral

$$\oint_S \boldsymbol{n}\cdot\boldsymbol{\sigma}\,dS$$

is called *the flux of tensor field* $\boldsymbol{\sigma}$ (less often the flux of tensor σ) across this surface. If the field is determined (and is continuously differentiated) also in the full volume V bounded by the closed surface S, then the *Gauss-Ostrogradsky's theorem* is valid:

$$\oint_S \boldsymbol{n}\cdot\boldsymbol{\sigma}\,dS=\int_V \mathrm{Div}\,\boldsymbol{\sigma}\,dV \tag{43.12}$$

—the flux of the tensor field across a closed surface is equal to the total divergence of the same tensor field in the volume bounded by this surface. The proof of the Gauss-Ostrogradsky theorem for tensor fields directly follows from the well-known proof of the theorem for vector fields and is therefore not given here.

Finally, *the curl of the tensor field* $\boldsymbol{\varepsilon}(\boldsymbol{r})$ is a pseudotensor curl ε of the same rank with components

$$(\mathrm{Curl}\,\boldsymbol{\varepsilon})_{il}=\delta_{ijk}\frac{\partial \varepsilon_{kl}}{\partial x_j}. \tag{43.13}$$

Curl $\boldsymbol{\varepsilon}$ can be regarded as a vector product: Curl $\boldsymbol{\varepsilon}=\nabla\times\varepsilon$. When it is necessary to differentiate ε with respect to the second index, Curl $\boldsymbol{\varepsilon}^*$ is used.

A differential operation of the second order is widely used in the mechanics of continuous media—the curl of a transposed curl of the tensor field $\boldsymbol{\varepsilon}(\boldsymbol{r})$. This tensor field

$$\mathrm{Inc}\,\boldsymbol{\varepsilon}=\mathrm{Curl}\,(\mathrm{Curl}\,\boldsymbol{\varepsilon})^* \tag{43.14}$$

has the same rank as the initial one and is called *the incompatibility of the tensor field* $\varepsilon(r)$. Its components are

$$(\mathrm{Inc}\,\varepsilon)_{ij} = \delta_{ikm}\delta_{jln}\frac{\partial^2\varepsilon_{mn}}{\partial x_k\,\partial x_l}. \tag{43.15}$$

Sec. 44. External Symmetry and Representation of Tensors and Pseudotensors

Matter tensors describe the properties of crystals. Let a Cartesian system of coordinates be connected with a crystal. A set of components of a matter tensor with respect to this system of coordinates characterizes numerically a corresponding property. Let us perform some orthogonal transformation of the coordinate system. The components of the matter tensor with respect to the new system of coordinates are not, generally speaking, equal to its respective components in the old system. If, however, a given transformation is included in the symmetry group of the crystal, then the components of the matter tensor with respect to the new system will coincide with those with respect to the old one. As a matter of fact, if the two systems of coordinates are connected by a transformation of crystal symmetry, their location with respect to the crystal is in essence the same. Consequently, *the matter tensor of the crystal is invariant with respect to all symmetry transformations of the crystal.*

Hence, the matter tensor of a crystal of definite symmetry cannot be quite arbitrary, it must satisfy certain requirements that follow from the crystal symmetry*. Let us formulate these requirements analytically. Let **A** be a matter tensor of rank r and $\| c_{i'k} \| = \| c_{i'k}(g) \|$ be a matrix of some transformation g of the symmetry of the crystal whose properties the tensor describes. Let us subject the crystal to transformation g. In the new system of coordinates the components of the tensor will be

$$A_{i'_1\ldots i'_r} = c_{i'_1k_1}\ldots c_{i'_rk_r}A_{k_1\ldots k_r}. \tag{44.1}$$

But since g is the transformation of the crystal symmetry, the tensor components in the new system of coordinates should coincide with its components in the old system. This can be written down as follows:

$$A_{i'_1\ldots i'_r} = \delta_{i'_1k_1}\ldots\delta_{i'_rk_r}A_{k_1\ldots k_r}. \tag{44.2}$$

Comparing (44.1) and (44.2) we obtain

$$(c_{i'_1k_1}\ldots c_{i'_rk_r} - \delta_{i'_1k_1}\ldots\delta_{i'_rk_r})\,A_{k_1\ldots k_r} = 0, \tag{44.3}$$

* These conditions imposed on matter tensors are necessary but by no means sufficient. The requirements of the thermodynamics of crystals as regards matter tensors are described in Chapter VII.

and these 3^r equalities must be fulfilled for any matrix $\| c_{i'k}(g) \|$ on the condition of g being one of the crystal symmetry transformations. Thus, equalities (44.3) are a system of linear equations that must be satisfied by the components of tensor **A**, if this tensor describes the properties of the crystal.

The number of equations in (44.3) is equal to the order of the crystal point group multiplied by 3^r, but there are much less independent equations among them: if tensor **A** satisfies equations (44.3) for matrices corresponding to the generators of the crystal point group, it will satisfy all the other equations too*. Indeed, if the tensor is invariant with respect to transformations g_1 and g_2, it is obviously also invariant with respect to all possible powers and products of these transformations.

Formula (44.3) should be somewhat changed for a matter pseudotensor **B**. In the new system of coordinates the pseudotensor **B** components are equal

$$B_{i'_1 \ldots i'_r} = \Delta c_{i'_1 k_1} \ldots c_{i'_r k_r} B_{k_1 \ldots k_r}, \tag{44.4}$$

where Δ is the determinant of the cosine matrix $\| c_{i'k} \|$. As to formula (44.2) it remains valid for pseudotensors. Comparing (44.2) and (44.4) we obtain, instead of (44.3)

$$(\Delta c_{i'_1 k_1} \ldots c_{i'_r k_r} - \delta_{i'_1 k_1} \ldots \delta_{i'_r k_r}) B_{k_1 \ldots k_r} = 0. \tag{44.5}$$

To begin with, let us consider the influence of the centre of symmetry in crystals, when it is available, on matter tensors. In this case the matter tensors should be invariant with respect to inversion. The cosine matrix, corresponding to inversion, is $c_{i'k} = -\delta_{i'k}$, its determinant is $\Delta = -1$. Substituting $c_{i'k}$ into (44.3) we obtain

$$[(-1)^r - 1]\, \delta_{i'_1 k_1} \ldots \delta_{i'_r k_r} A_{k_1 \ldots k_r} = 0. \tag{44.6}$$

The result depends on whether the rank r of the tensor is even or odd. With an even r we have an identity

$$0 \cdot A_{i'_1 \ldots i'_r} = 0,$$

which is satisfied with any tensor **A**. Thus, all even-rank tensors are invariant with respect to inversion, or, in other words, are centrosymmetric. With an odd r

$$-2A_{i'_1 \ldots i'_r} = 0.$$

This means that if a crystal has a centre of symmetry, all the odd-rank matter tensors vanish, in other words, *centrosymmetric crystals have no properties specified by odd-rank tensors.*

---

* See Sec. 5 for point group generators

If a pseudotensor, and not a tensor, is discussed, then due to the availability of factor Δ in (44.5), equal, in case of inversion, to -1, r in (44.6) will have to be replaced by $r+1$. Therefore all the odd-rank matter pseudotensors are centrosymmetric; on the contrary, all even-rank matter pseudotensors in centrosymmetric crystals vanish.

In connection with the resulting solution of this problem it would be expedient to introduce a new classification of tensors. True tensors of an even rank and pseudotensors of an odd rank are called *even-type tensors*; it has been shown that they are all invariant with respect to inversion. True odd-rank tensors and even-rank pseudotensors are called *odd-type tensors*: under inversion the signs of all their components are reversed. In discussing the duality relations (Sec. 42) we saw that one and the same quantity can be regarded as a true tensor and as a pseudotensor. Therefore, when we say that a certain quantity is for example a pseudotensor, we describe essentially not the quantity itself but the manner of its notation. On the contrary, being even or odd is an essential property of a quantity. For instance, small rotations of a continuous medium (see Sec. 49) can be specified both by an axial vector $\overset{\circ}{\boldsymbol{\varphi}}$ and by an antisymmetric second-rank dual tensor $\boldsymbol{\omega}$, but in both notations of this quantity we use tensors of one and the same, and, more specifically, of an even type.

Since all even-type matter tensors are centrosymmetric by their nature, they "do not feel" whether a crystal has a centre of symmetry or not. If we mentally add inversion to crystal symmetry operations (as well as the products of inversion by all symmetry operations), this will impose no new restrictions on the kind of an even-type matter tensor. Hence, as regards the symmetry of properties described by even-type tensors crystals are divided not into the crystallographic classes, but only into the Laue classes or subsystems (we remember that the point groups of all the non-centrosymmetric classes in a given subsystem pass into a point group of the only centrosymmetric class of the same subsystem upon addition of inversion to their generators, see Sec. 6). Thus, there are no more than 11 varieties of symmetry of even-type properties in all possible crystals, and no more than 14 if the media of limit symmetry are taken into account.

Only non-centrosymmetric crystals can have odd-type properties, as has already been noted; therefore the number of the symmetry varieties of these properties does not exceed the number of non-centrosymmetric crystallographic point groups, i.e. 21; when limit groups are taken into account, the number increases to 25.

The matter tensor of a crystal is invariant with respect to all the symmetry transformations of the crystal, but, generally speaking, not only to them. For instance, an even-type matter tensor is invariant with respect to inversion even when the crystal whose

property it describes is non-centrosymmetric. On the other hand, in the analysis of different crystal-physical situations with the aid of the Curie principle it is necessary to know the symmetry operations, with respect to which one or another field tensor is invariant. A. V. Shubnikov introduced a concept of *tensor symmetry* which is applicable both to the matter and field tensors* (later it was called *external symmetry* in distinction from the internal symmetry): the group of tensor external symmetry is the totality of all orthogonal transformations with respect to which a given tensor is invariant.

A direct method of the determination of external symmetry was suggested by L. I. Sedov and V. V. Lokhin**. They consider a set of the principal formulas of the theory of the external symmetry of tensors (44.3) as a system of equations in matrix elements $c_{i'k}$, and they regard tensor **A** as specified. Every solution of this system is a transformation matrix with respect to which tensor **A** is invariant. Non-orthogonal matrices can occur among those satisfying equation (44.3); according to the definition of the tensor external symmetry they are not to be considered. The remaining orthogonal matrices constitute the external symmetry group of tensor **A**.

In principle this method permits finding the external symmetry group of any tensor specified by its components in an arbitrary system of coordinates, but it cannot be easily used: equations (44.3) are linear only with respect to components of tensor $A_{k_1} \ldots A_{k_r}$, while with respect to matrix elements $c_{i'k}$ they are equations of r-th degree (r is the tensor rank).

L. I. Sedov and V. V. Lokhin proved that any crystallographic and limit group can be defined as an external symmetry group of a certain tensor or as an intersection (a common part) of external symmetry groups of several tensors.

The matter tensors of crystals depend on temperature, frequency and other scalar parameters. Therefore, theoretical crystal physics discussed, along with the external symmetry of matter tensors, also the external symmetry of *matter tensor-functions*—the tensor-functions of scalar parameters***. To different sets of scalar parameters $\omega_1, \omega_2, \ldots$ there correspond different matter tensors $\mathbf{A}(\omega_1)$, $\mathbf{A}(\omega_2) \ldots$. Their symmetry groups $G(\mathbf{A}(\omega_1))$, $G(\mathbf{A}(\omega_2)) \ldots$ contain, as a rule, the same symmetry elements, but their orientation can be different in different tensors. *The group of external symmetry* $G^{(\omega)}(\mathbf{A})$ of a matter tensor-function $\mathbf{A}(\omega)$ is the intersection (com-

---

* Shubnikov (1949). See also Zheludev (1957) and Koptsik (1958).

** Lokhin and Sedov (1963) or Sedov (1970), Appendix 1. See also Maloletkin and Fomin (1972). Lokhin and Sedov consider the whole group of transformations determined by the given tensor, even if it includes non-orthogonal transformations (strain, shear, etc). However, we restrict ourselves with a discussion of the orthogonal subgroup of this group. Cf. Vakulenko (1972).

*** See also Koptsik (1966) on the symmetry of tensor-functions.

mon part) of these groups:

$$G^{(\omega)}(\mathbf{A}) = G(\mathbf{A}(\omega_1)) \cap G(\mathbf{A}(\omega_2)) \cap \ldots = \bigcap_i G(\mathbf{A}(\varphi_i)). \qquad (44.7)$$

Group $G^{(\omega)}(\mathbf{A})$ of the external symmetry of the tensor-function $\mathbf{A}(\omega)$ includes those, and only those, transformations which transfer tensor $\mathbf{A}$ into itself at any values of the parameters. On the other hand, according to Neumann's principle, all elements of the point group of crystal symmetry G should be included in the external symmetry groups of all matter tensors of this crystal, and, consequently, in the symmetry groups of the matter tensor-functions. Hence the relation, derived by Koptsik (1966), between the symmetry groups of crystal G, of the matter tensor $G(\mathbf{A})$ and the matter tensor-function $G^{(\omega)}(\mathbf{A})$:

$$G(\mathbf{A}) \supseteq G^{(\omega)}(\mathbf{A}) \supseteq G. \qquad (44.8)$$

Let us consider some examples. All the matter vectors of crystals that have a symmetry axis are directed along this axis, and therefore the symmetry not only of each individual matter vector but also of the sets of all imaginable matter vectors equals ∞m. But matter vectors of a class m crystal can have any direction that lies in the symmetry plane, and therefore, even though the symmetry of each individual vector is still ∞m, the symmetry of their totality is only m.

Similarly, each individual matter tensor $[V^2]$ of a crystal of any class of the monoclinic system has the mmm symmetry, but the whole set of such tensors has only one common two-fold symmetry axis and one common symmetry plane, so that the symmetry group of this set is $2/m$.

Let us discuss some methods of the representation of tensors and pseudotensors of an arbitrary rank. In Sec. 22 are described two types of surfaces representing second-rank symmetric tensors: characteristic and representation surfaces. Only the latter are mostly used for representing higher-rank tensors. In polar coordinates the equation of the representation surface of a symmetric p-rank tensor $\mathbf{T}$ is

$$r(\vartheta, \varphi) = T_{i_1 \ldots i_p} n_{i_1} \ldots n_{i_p} \qquad (44.9)$$

$$(n_1 = \sin\vartheta \cos\varphi, \quad n_2 = \sin\vartheta \sin\varphi, \quad n_3 = \cos\vartheta).$$

If we substitute into this equation the components of a tensor or a pseudotensor $\mathbf{A}$ whose internal symmetry is not equal to $[V^p]$ or $\varepsilon[V^p]$, only its symmetric part $T_{i_1 \ldots i_p} = A_{(i_1 \ldots i_p)}$ will influence the shape of the representation surface, since

$$\mathbf{A}_{i_1 \ldots i_p} n_{i_1} \ldots n_{i_p} = T_{i_1, \ldots i_p} n_{i_1} \ldots n_{i_p}.$$

As was already noted (Secs. 22, 24) a representation surface can consist of white (positive) and black (negative) parts: the former correspond to the positive values of r, the latter to its negative values. Some of the surfaces shown in Sec. 24 are representation surfaces of the higher-rank tensors. For instance, the surfaces of an extension coefficient (see Figs. 24.5-24.11) are in essence the representation surfaces of a fourth-rank matter tensor $s_{ijkl}^{\{4\}} = s_{(ijkl)}$, where s is the tensor of the elastic compliance coefficients (see Secs. 51-53), while the surfaces of the twist coefficient (Figs. 24.6, 24.10, 24.11)

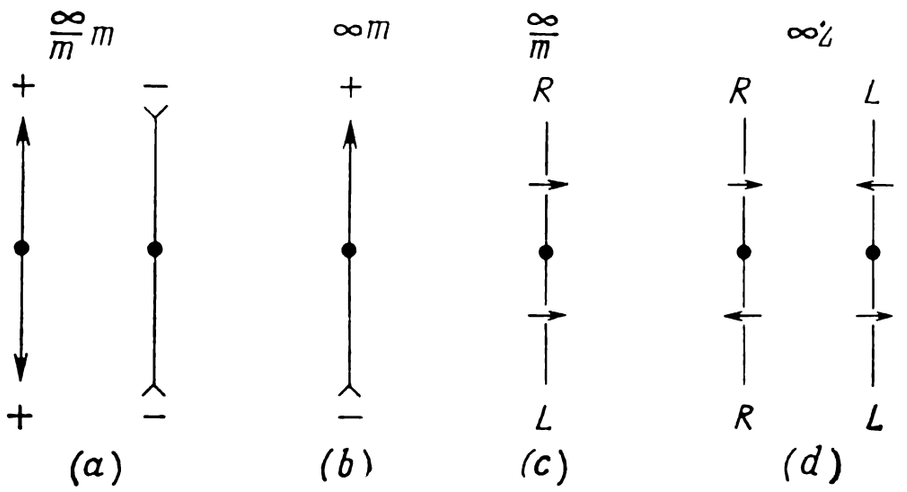


Fig. 44.1. Diameters of representation surfaces: (a) of an even-type true tensor, (b) of an odd-type true tensor, (c) of an even-type pseudotensor, (d) of an odd-type pseudotensor. The diameters (b), (c) and (d) are the polar, axial and screw directions respectively. Dots show the centres of representation surface. The plus and minus signs correspond to the white and black colours of the surface at the end of a given diameter, while letters R and L correspond to right-hand and left-hand rotations. (Cf. Shubnikov (1958, Fig. 117) and Shubnikov and Koptsik (1972, Fig. 74)

are the representation surfaces of a matter tensor $Q_{ijkl} = 2\,(Z_{(ik)}\delta_{(jl)} - s_{(ijkl)})$ where $Z_{ik} = s_{imkm}$ (cf. formulas (54.20) and (54.21)). Many such surfaces, their sections and their stereographic projections (Sec. 24) are given in subsequent chapters: Figs. 54.3-54.10, 56.4, 58.1-58.3, 75.1, etc.

Let us compare the representation surfaces of even- and odd-type tensors. Since even-type tensors are centrosymmetric, their representation surfaces are also centrosymmetric: $r\,(\boldsymbol{n}) = r\,(-\boldsymbol{n})$. Therefore any diameter of the representation surface of an even-type tensor consists of two radii equal in magnitude and corresponding to one and the same sign (Fig. 44.1*a*); its symmetry is ∞/mm.

Tensors of the odd type are anticentrosymmetric: under inversion their sign is reversed*; such are also their representation surfaces:

* The antisymmetry of these surfaces is connected with this circumstance, see Secs. 67, 68.

$r(\boldsymbol{n}) = -r(-\boldsymbol{n})$. Any diameter of such a representation surface consists of two radii also equal in magnitude but corresponding to opposite signs (Fig. 44.1*b*); its symmetry is ∞m. The directions in a crystal whose symmetry does not exceed ∞m are called *polar* (see Sec. 3 and Appendix C). It follows from the Curie principle that

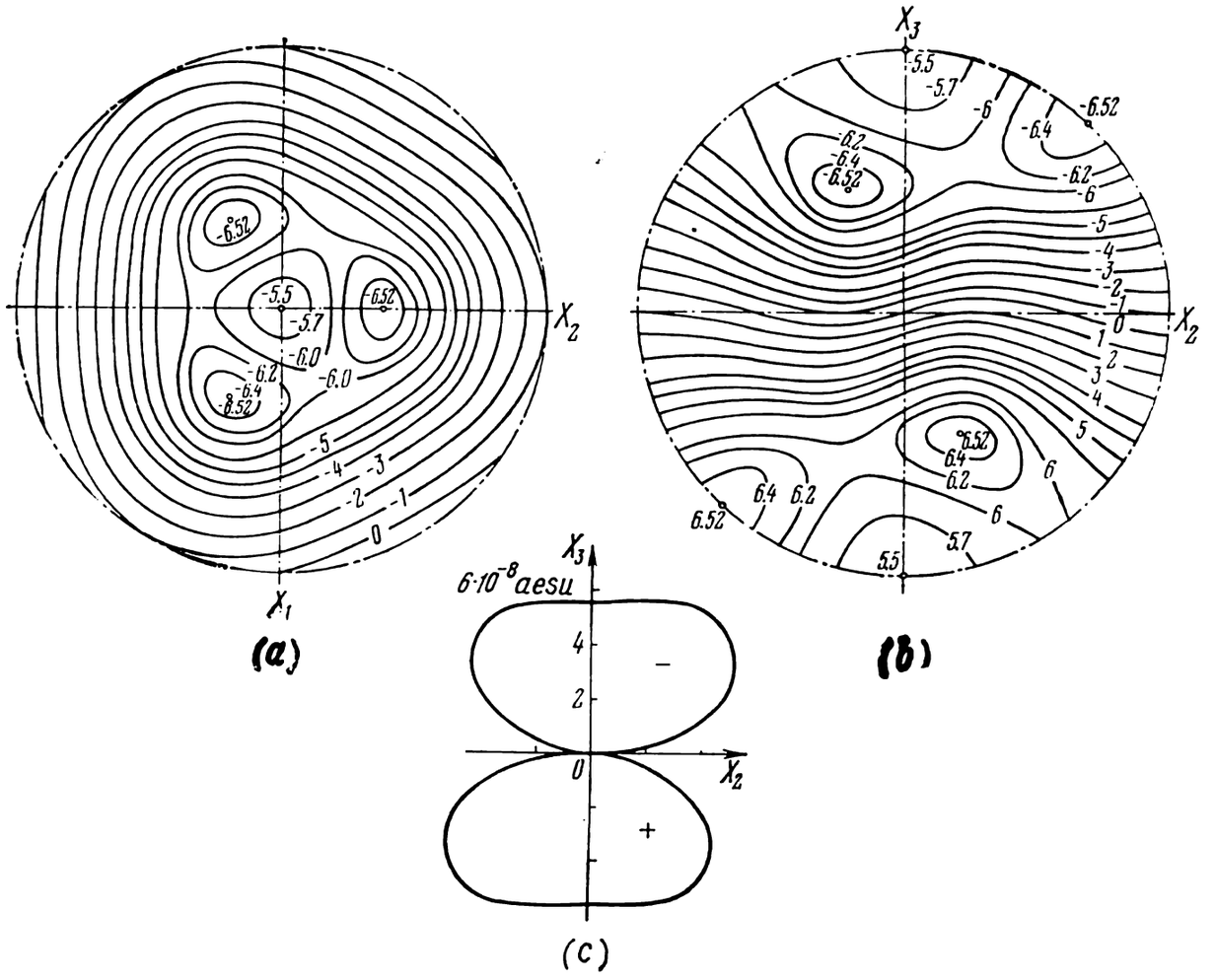


Fig. 44.2. Representation surface of the longitudinal piezoelectric effect in a tourmaline crystal (class $3m$)—an example of the representation surface of an odd-type tensor: (a) stereographic projection, axis X_3 [0001] is in the centre of projection; (b) ditto, but with axis X_1 [$2\bar{1}\bar{1}0$] in the centre of projection, in 10^{-8} aesu. (c) section of the representation surface by plane X_2X_3 ($2\bar{1}\bar{1}0$). Surface symmetry group $\bar{3}m$, antisymmetry group $3'm$ (see Sec. 68) (Butabayev and Sirotin, 1973).

the diameters of the representation surfaces of odd-type matter tensors can differ from zero only in the directions which are polar in the given crystal. Two stereographic projections and a section of the surface of the longitudinal piezoelectric effect in a tourmaline crystal (class $3m$) are shown in Fig. 44.2. This is the representation surface of a third-rank matter tensor $f_{ijk} = d_{(ijk)}$, where **d** is the tensor of piezoelectric coefficients (see Sec. 58).

The representation surfaces of symmetric pseudotensors are also described by equation (44.9), but the radius-vectors of these surfaces are apparently transformed not according to a vector law but in accordance with a pseudovector law, i.e. they are axial vectors. Therefore to each point of the representation surface of a pseudotensor there is assigned not a sign (as to the points of the representation surfaces of true tensors) but rotation in the direction of the rotation of the axial radius-vector of the given point. Let us agree to call the given point of the representation surface of a pseudotensor a *right-hand* one, if, when viewed from the external side of the surface, the rotation appears to be counterclockwise (correspondingly, when viewed from the inside, i.e. along the radius-vector, it appears to be clockwise), and *left-hand* one in the opposite case.

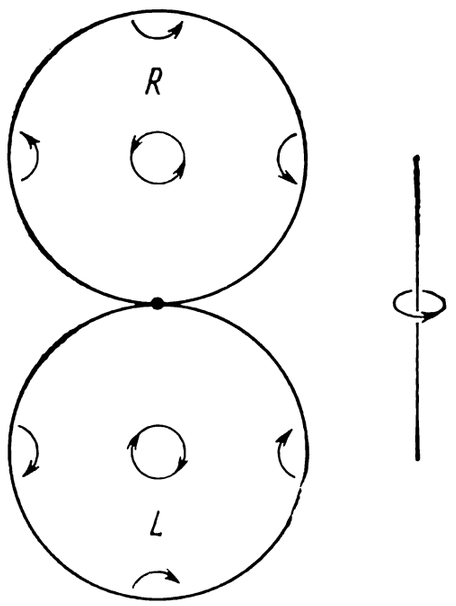


Fig. 44.3. Representation surface of an axial vector—an example of the representation surface of an even-type pseudotensor. Surface symmetry is ∞/m. Circular arrows show the direction of rotation. Letters R and L mark those parts of the surface that consist of right- and left-hand points respectively. On the right is an axial vector of a corresponding length and direction. Compare with the representation surface of a polar vector, Fig. 22.3

Now let us compare the representation surfaces of pseudotensors of the even and odd types. The representation surfaces of the even-type pseudotensors (i.e. of an odd rank) are centrosymmetric, this meaning that each diameter of such a surface consists of two radii of equal length and the same direction of rotation (Fig. 44.1); its symmetry is ∞/m. The directions in crystals whose symmetry does not exceed ∞/m are called *axial*, so that the diameters of the representation surfaces of matter pseudotensors of the even type differ from zero only in axial directions. An example of such a surface is shown in Fig. 44.3.

The diameters of the representation surfaces of the odd-type pseudotensors consist of radii of equal length and opposite directions of rotation (see Fig. 44.1*d*); their symmetry is $\infty 2$. The directions of this and lower symmetry in crystals are called *screw directions*—the diameters of the representation surfaces of matter pseudotensors of the odd type differ from zero only in the screw directions. An example of a representation surface of an odd-type pseudotensor is shown in Fig. 44.4. This is the representation surface of a second-rank pseudotensor of symmetry $\bar{4}2m$, whose matrix in the $X_1X_2X_3$

system is

$$\|G_{ij}\| = \begin{Vmatrix} -G & 0 & 0 \\ 0 & G & 0 \\ 0 & 0 & 0 \end{Vmatrix}, \tag{44.10}$$

if the right-hand rotation is given the minus sign and the left-hand one the plus sign. This pseudotensor describes the optical activity of crystals of classes $\bar{4}2m$, $\bar{4}$, $mm2$ and m, in particular the rotation of the plane of polarization of light in crystals of $\bar{4}2m$ and $\bar{4}$ classes when the principal refractive indices N_o and N_e coincide (see Sec. 81)*.

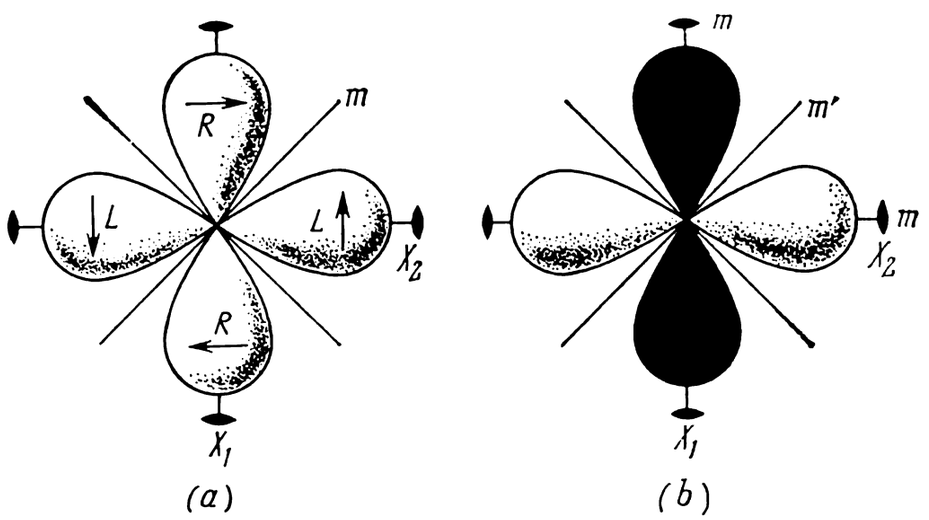


Fig. 44.4. Representation surfaces of: (a) a symmetric second-rank pseudotensor, symmetry $\bar{4}2m$, (b) a symmetric second-rank tensor with the same components, its symmetry is mmm, antisymmetry $4'/mmm'$, see Sec. 68 (after Shubnikov, (1951))

If all components of a true tensor and pseudotensor of the same rank having the same name coincide, their representation surfaces have the same outlines. However, since the radius-vectors forming these two surfaces have different sense and different symmetry, the sense and symmetry of the surfaces themselves are also different. This can be seen, for instance, from a comparison of the representation surfaces of a polar vector (Fig. 22.3) and an axial vector (Fig. 44.3). Another example is this: the same outlines as those shown in Fig. 44.4*a* of the representation surface of a second-rank

* To the right-hand rotation there correspond in our definition the right-hand parts of the representation surface. In accordance with a definition used in optics, when a polarization plane is rotated in the direction of a right-hand screw, the rotation is considered to be left-hand (see Sec. 81) and corresponds to the negative values of the normal component of pseudotensor G_{ij}. The choice of the sign in the matrix (44.10) conforms to this.

pseudotensor of symmetry $\bar{4}2m$, has the representation surface of a true second-rank tensor whose components are defined by the same matrix (44.10) (Fig. 44.4*b*). However the symmetry of this tensor and of its representation surface is entirely different: it is the *mmm* group, as for any symmetric second-rank tensor with three different eigenvalues ($-G$, G and 0)*.

Thus the symmetry of the representation surfaces can be correctly defined only when it is remembered that the points constituting them have a certain colour (a sign) or a direction of rotation, i.e. that these surfaces represent, according to A. V. Shubnikov (1951), material figures.

Sec. 45. Method of Direct Verification

In this Section there is shown the most convenient method of derivation of the necessary conditions that are to be satisfied by a tensor invariant with respect to reflection in a symmetry plane, to rotation about two- and four-fold axes as well as about three-fold axes available in the cubic system crystals. It was suggested by Fumi (1952) and is called *the method of direct verification.*

In this method essential use is made of two circumstances: (1) tensor components transform as products of vector components; (2) we are concerned with the form of a matter tensor in the crystal-physical system of coordinates which is constructed on the symmetry elements of a crystal, so that the symmetry axes and the normals to the symmetry plane coincide with the coordinate axes, with the bisectrices of the angles between them and so on.

Let us now consider how vector components are transformed when the coordinate system is turned through 90° about axis X_3. If we denote the mutually orthogonal unit vectors of the "old" coordinate system $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$, and those of the "new" one $\boldsymbol{e}_{1'}$, $\boldsymbol{e}_{2'}$, $\boldsymbol{e}_{3'}$, we can write

$$x\boldsymbol{e}_1 + y\boldsymbol{e}_2 + z\boldsymbol{e}_3 = x'\boldsymbol{e}_{1'} + y'\boldsymbol{e}_{2'} + z'\boldsymbol{e}_{3'}$$

Here x, y, z are the first, second and third vector components respectively.

The cosine matrix for this rotation is

$$\| c_{i'k} \| = \begin{Vmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{Vmatrix}.$$

The new mutually orthogonal unit vectors determined by formula $\boldsymbol{e}_{i'} = c_{i'k}\boldsymbol{e}_k$ are respectively $\boldsymbol{e}_{i'} = \boldsymbol{e}_2$, $\boldsymbol{e}_{2'} = -\boldsymbol{e}_1$, $\boldsymbol{e}_{3'} = \boldsymbol{e}_3$.

* The antisymmetry group of this tensor and of its representation surface is $4'/mmm'$ (see Secs. 67, 68).

Thus

$$xe_1 + ye_2 + ze_3 = x'e_2 - y'e_1 + z'e_3.$$

Since the unit vectors are linearly independent, this equality holds only when

$$x' = y, \quad y' = -x, \quad z' = z.$$

(The same result could be obtained at once if matrix $\| c_{i'k} \|$ were applied directly to the components and not to the unit vectors; we have chosen a longer path in order to perform similar operations on cyclic coordinates (see the next Section), which in distinction from the Cartesian ones transform differently from the corresponding cyclic basic vectors.) We see that in this case the vector component either remains unchanged or passes into another component, perhaps also changing its sign. This is explained by the type of the cosine matrix: all its elements are integers and are +1, —1 or 0. Fumi's method of direct verification is applied only to such symmetry operations which are characterized by integral cosine matrices.

The cosine matrix is integral only for some "choice" rotations whose axes are located in a strictly definite manner with respect to the coordinate system. For instance, for the rotation through 120° (three-fold axis) the cosine matrix is integral if the rotation axis makes up equal angles with axes X_1, X_2 and X_3, but it is not integral if this axis coincides with any of the coordinate axes. Table 45.1 gives all practically important cases of such rotations.

Table 45.1

Transformations of Indices Used in the Method of Direct Verification

g	$\bar{1}$	2_z	2_x	2_y	2_{xy}	m_z	m_x	m_y	m_{xy}	4_z	$\bar{4}_z$	3_{xyz}
x'	$-x$	$-x$	x	$-x$	y	x	$-x$	x	$-y$	y	$-y$	y
y'	$-y$	$-y$	$-y$	y	x	y	y	$-y$	$-x$	$-x$	x	z
z'	$-z$	z	$-z$	$-z$	$-z$	$-z$	z	z	z	z	$-z$	x

Note. Indices x, y, z mean that the symmetry axis (or the perpendicular to the symmetry plane) coincides with the axes X_1, X_2, X_3 respectively. Index xy shows that the axis (or perpendicular) is directed along the bisectrix of the angle between axes X_1 and X_2, while index xyz shows that it is directed along a straight line forming equal angles with the axes X_1, X_2, X_3.

Now let us consider how the components of a second-rank tensor transform under the same rotation. To make use of the fact that they transform as the products of a vector components we shall denote a component with indices 11 by symbol $[xx]$, with indices 12 by symbol $[xy]$ and so on. Since we do not assume that the tensor is

symmetric with respect to indices (e.g. $[xy] \neq [yx]$), it is necessary to be careful about the sequence of the "factors" by no means permuting them arbitrarily. For the rest, these symbols can be used as ordinary products. If under operation 4_z the vector components are transformed in the following way

$$x' = y, \quad y' = -x, \quad z' = z,$$

then the tensor components, as their products, are transformed as follows:

$$\begin{aligned}
[xx]' &= [yy], & [yx]' &= -[xy], & [zx]' &= [zy],\\
[xy]' &= -[yx], & [yy]' &= [xx], & [zy]' &= -[zx],\\
[xz]' &= [yz], & [yz]' &= -[xz], & [zz]' &= [zz].
\end{aligned}$$

Having done the same for operations 2_z, 2_x and 3_{xyz}, we compose a table:

g	2_z	2_x	4_z	3_{xyz}	g	2_z	2_x	4_z	3_{xyz}
$[xx]'$	$[xx]$	$[xx]$	$[yy]$	$[yy]$	$[zx]'$	$-[zx]$	$-[zx]$	$[zy]$	$[xy]$
$[yy]'$	$[yy]$	$[yy]$	$[xx]$	$[zz]$	$[xz]'$	$-[xz]$	$-[xz]$	$[yz]$	$[yx]$
$[zz]'$	$[zz]$	$[zz]$	$[zz]$	$[xx]$	$[xy]'$	$[xy]$	$-[xy]$	$-[yx]$	$[yz]$
$[yz]'$	$-[yz]$	$[yz]$	$-[xz]$	$[zx]$	$[yx]'$	$[yx]$	$-[yx]$	$-[xy]$	$[zy]$
$[zy]'$	$-[zy]$	$[zy]$	$-[zx]$	$[xz]$					

If a crystal belongs to class 2 and its twofold axis is parallel to X_3, then the components of the matter tensor should not change under operation 2_z. Therefore we may equate the indices in the same rows of the first and second columns of our table. But such equalities as $[yz] = -[yz]$ are satisfied only for $[yz] = 0$, while trivial equalities, such as $[xx] = [xx]$ are satisfied at any values of the corresponding components. Thus, the second-rank matter tensor for the crystals of class 2 (at a non-standard orientation of the twofold axis parallel to X_3) is

$$\| T_{ij} \| = \begin{Vmatrix} T_{11} & T_{12} & 0 \\ T_{21} & T_{22} & 0 \\ 0 & 0 & T_{33} \end{Vmatrix}.$$

The discussed tensor is of the even type and therefore, as was shown in the preceding Section, it should have exactly the same form for crystals of other classes of the same subsystem: m and $2/m$.

Let us now discuss class 4. Since 2_z is among the operations of group 4, we can at once assume the components $[yz]$, $[zy]$, $[zx]$ and

$[xz]$ to be zero*. For the other components we have $[xx] = [yy]$, $[xy] = -[yx]$. So, for class 4 (as well as for classes $\bar{4}$ and $4/m$) the matter tensor of the second rank is

$$\|T_{ij}\| = \begin{Vmatrix} T_{11} & T_{12} & 0 \\ -T_{12} & T_{11} & 0 \\ 0 & 0 & T_{33} \end{Vmatrix}.$$

We have considered groups with one generator. For groups with several generators the condition for the equality of transformed and non-transformed components must hold for each generator individually. Table 45.2 shows the sets of generators most convenient for the application of the method of direct verification.

Table 45.2

Generators of Crystallographic and Limit Groups

Group	Generators	Group	Generators
$\bar{1}$	$\bar{1}$	$4mm$	$4_z,\ m_x$
$2\ (2 \parallel X_2)$	2_y	$\bar{4}2m\ (2 \parallel X_1)$	$\bar{4}_z,\ 2_x$
$2\ (2 \parallel X_3)$	2_z	$\bar{4}m2\ (m \perp X_1)$	$\bar{4}_z,\ m_x$
$m\ (m \perp X_2)$	m_y	$4/mmm$	$4_z,\ 2_x,\ \bar{1}$
$m\ (m \perp X_3)$	m_z	6	6_z
$2/m\ (2 \parallel X_2)$	$2_y,\ \bar{1}$	$\bar{6}$	$\bar{6}_z$
$2/m\ (2 \parallel X_3)$	$2_z,\ \bar{1}$	$6/m$	$6_z,\ \bar{1}$
222	$2_z,\ 2_x$	622	$6_z,\ 2_x$
$mm2$	$2_z,\ m_x$	$6mm$	$6_z,\ m_x$
mmm	$2_z,\ 2_x,\ \bar{1}$	$\bar{6}m2\ (m \perp X_1)$	$\bar{6}_z,\ m_x$
3	3_z	$\bar{6}2m\ (2 \parallel X_1)$	$\bar{6}_z,\ 2_x$
$\bar{3}$	$3_z,\ \bar{1}$	$6/mmm$	$6_z,\ 2_x,\ \bar{1}$
$32\ (2 \parallel X_1)$	$3_z,\ 2_x$	23	$2_z,\ 3_{xyz}$
$32\ (2 \parallel X_2)$	$3_z,\ 2_y$	$m3$	$2_z,\ 3_{xyz},\ \bar{1}$
$3m\ (m \perp X_1)$	$3_z,\ m_x$	432	$4_z,\ 3_{xyz}$
$3m\ (m \perp X_2)$	$3_z,\ m_y$	$\bar{4}3m$	$\bar{4}_z,\ 3_{xyz}$
$\bar{3}m\ (2 \parallel X_1)$	$3_z,\ 2_x,\ \bar{1}$	$m3m$	$4_z,\ 3_{xyz},\ \bar{1}$
$\bar{3}m\ (2 \parallel X_2)$	$3_z,\ 2_y,\ \bar{1}$	∞	∞_z
4	4_z	∞/m	$\infty_z,\ \bar{1}$
$\bar{4}$	$\bar{4}_z$	$\infty 2$	$\infty_z,\ 2_x$
$4/m$	$4_z,\ \bar{1}$	∞m	$\infty_z,\ m_x$
422	$4_z,\ 2_x$	∞/mm	$\infty_z,\ 2_x,\ \bar{1}$

* It is possible to do without it. For instance, comparing equalities $[yz] = [xz]$ and $[xz] = -[yz]$, we immediately see that $[yz] = [xz] = 0$.

We shall take advantage of this rule to define the form of the second-rank matter tensor for classes 222, 422, 23 and 432 (and thus for all classes of the corresponding subsystems).

For class 222 there remain, after verification for invariance with respect to 2_z, the components $[xx]$, $[yy]$, $[zz]$, $[xy]$, and $[yx]$. The verification for invariance with respect to 2_x eliminates the last two components. As a result we obtain

$$\| T_{ij} \| = \begin{Vmatrix} T_{11} & 0 & 0 \\ 0 & T_{22} & 0 \\ 0 & 0 & T_{33} \end{Vmatrix}.$$

For class 422 there remain, after verification for invariance with respect to 4_z, $[xx] = [yy]$, $[zz]$, $[xy] = -[yx]$. The verification for invariance with respect to 2_x eliminates the last pair of components, so that

$$\| T_{ij} \| = \begin{Vmatrix} T_{11} & 0 & 0 \\ 0 & T_{11} & 0 \\ 0 & 0 & T_{33} \end{Vmatrix}.$$

For class 23, examining the effect of operation 3_{xyz} on the components that remained after the verification for 2_z, we obtain equalities $[xx] = [zz] = [yy]$, $[xy] = [zx] = 0$, $[yx] = [xz] = 0$. Hence

$$\| T_{ij} \| = \begin{Vmatrix} T_{11} & 0 & 0 \\ 0 & T_{11} & 0 \\ 0 & 0 & T_{11} \end{Vmatrix}.$$

Having examined the effect of operation 3_{xyz} on the components that remained after the verification for 4_z, we obtain the same result for class 432.

The discussed example shows that, first, the group of the external symmetry of a tensor may be much broader than the group of crystal symmetry with respect to which a given tensor should be invariant (the point is not only that a centre of symmetry is added: having applied the requirements for invariance with respect to group 23 to the tensor, we obtained a tensor of not the $m3$ external symmetry, but of a much higher one $-\infty\infty m$).

The discussed example shows, second, the connection between the external and internal symmetry of a tensor. We considered a tensor of internal symmetry V^2, i.e. we did not assume its being symmetric (or antisymmetric) in indices. For the Laue classes $2/m$ and $4/m$ we therefore obtained a tensor of internal symmetry V^2, but for the Laue classes mmm, $4/mmm$, $m3$ and $m3m$ the conditions for invariance resulted in raising the internal symmetry of the tensor to $[V^2]$—it became symmetric with respect to indices. Thus the

external symmetry of a tensor sometimes predetermines its internal symmetry.

The method of direct verification can be applied just as simply to tensors of higher ranks. The only trouble is that they have more components, so that the solution of the problem becomes much longer, even though not more difficult. This trouble can be avoided to a certain degree, by not writing out all the permutations of indices: it is obvious for instance, that if $[xz]' = [yz]$ then $[zx]' = [zy]$.

Let us discuss a third-rank tensor and find out what it is for crystals of classes $\bar{4}2m$ and 422. It will suffice to see the influence on it of generators 4_z and 2_x for class $\bar{4}2m$ and 4_z and 2_x for class 422 (see Table 45.2). Therefore we compile a Table:

g	2_x	$\bar{4}_z$	4_z	g	2_x	$\bar{4}_z$	4_z
$[xxx]'$	$[xxx]$	$-[yyy]$	$[yyy]$	$[yyz]'$	$-[yyz]$	$-[xxz]$	$[xxz]$
$[yyy]'$	$-[yyy]$	$[xxx]$	$-[xxx]$	$[yyx]'$	$[yyx]$	$-[xxy]$	$[xxy]$
$[zzz]'$	$-[zzz]$	$-[zzz]$	$[zzz]$	$[zzx]'$	$[zzx]$	$-[zzy]$	$[zzy]$
$[xxy]'$	$-[xxy]$	$[yyx]$	$-[yyx]$	$[zzy]'$	$-[zzy]$	$[zzx]$	$-[zzx]$
$[xxz]'$	$-[xxz]$	$-[yyz]$	$[yyz]$	$[xyz]'$	$[xyz]$	$[yxz]$	$-[yxz]$

The requirement of invariance with respect to 2_x results in the vanishing of the components $[yyy]$, $[zzz]$, $[xxy]$, $[xxz]$, $[yyz]$, $[zzy]$, as well as of all the components differing from them only by the permutation of indices. We verify the remaining components for invariance with respect to 4_z and obtain $[xxx] = [yyy] = 0$, $[yyx] = [xxy] = 0$, $[zzx] = [zzy] = 0$, $[xyz] = [yxz]$, the latter equality holding after any rearrangement of indices performed simultaneously in its left- and right-hand sides. Thus, in tensor **g** of internal symmetry V^3 invariant with respect to group $\bar{4}2m$ only the following components survive:

$$g_{123} = g_{213}, \quad g_{231} = g_{132}, \quad g_{312} = g_{321},$$

only six components, three of which are independent. For tensor **d** with internal symmetry $V\,[V^2]$ whose components satisfy the equality $d_{ikl} = d_{ilk}$, the number of independent components diminishes to two:

$$d_{123} = d_{213} = d_{231} = d_{132}, \quad d_{312} = d_{321}.$$

Finally, tensor **f** with internal symmetry $[V^3]$ has only one independent component:

$$f_{123} = f_{213} = f_{231} = f_{132} = f_{312} = f_{321}.$$

For finding third-rank tensors invariant with respect to group 422 we shall verify the components, not eliminated by operation 2_x

for invariance with respect to 4_z. We obtain equalities

$$[xxx] = -[yyy] = 0, \quad [yyx] = -[xxy] = 0$$
$$[zzx] = -[zzy] = 0, \quad [xyz] = -[yxz].$$

Reasoning as before, we see that tensors **g** of internal symmetry V^3 invariant with respect to group 422 have six non-zero components

$$g_{123} = -g_{213}, \quad g_{231} = -g_{132}, \quad g_{312} = -g_{321}$$

three of them being independent. Tensors **d** of internal symmetry V $[V^2]$ have only four such components

$$d_{123} = d_{132} = -d_{213} = -d_{231}$$

one of them being independent. Finally, tensors of internal symmetry $[V^3]$ vanish identically.

So the form of matter tensors of any rank for the crystals of the monoclinic, rhombic, tetragonal and cubic systems is determined almost without any calculations. 25 types of matter tensors and pseudotensors, from the zero to the sixth rank inclusive are given in Appendix E.

Sec. 46. Cyclic Coordinates. Hermann's Theorem

The method of direct verification described in the preceding Section does not make it possible to find tensors invariant with respect to the groups of the trigonal and hexagonal systems, as well as with respect to the limit groups of symmetry. The solution of these problems calls for more complicated methods, one of which is the method of direct verification in cyclic coordinates which we shall discuss here.

Let us consider cyclic basic vectors.

$$\boldsymbol{j} = \frac{1}{2}(\boldsymbol{e}_1 + i\boldsymbol{e}_2), \quad \bar{\boldsymbol{j}} = \frac{1}{2}(\boldsymbol{e}_1 - i\boldsymbol{e}_2), \quad \boldsymbol{e} = \boldsymbol{e}_3. \tag{46.1}$$

Two of them are imaginary and complex conjugate, a bar over vector $\bar{j}$* being reminiscent of this. They are, however, linearly independent, since

$$(\boldsymbol{j} \times \bar{\boldsymbol{j}}) \cdot \boldsymbol{e} = -\frac{1}{2} i \neq 0,$$

and can therefore be used as a basis. The conversion of (46.1) is

$$\boldsymbol{e}_1 = \boldsymbol{j} + \bar{\boldsymbol{j}}, \quad \boldsymbol{e}_2 = -i(\boldsymbol{j} - \bar{\boldsymbol{j}}), \quad \boldsymbol{e}_3 = \boldsymbol{e}. \tag{46.2}$$

* All the operations on complex vectors are performed in the same way as on real ones, i being regarded as an ordinary coefficient (i^2 being equal to -1). It should be noted that in linear algebra the scalar product of complex vectors is determined differently.

Let us write out one and the same real vector in the Cartesian and cyclic bases:

$$x\boldsymbol{e}_1 + y\boldsymbol{e}_2 + z\boldsymbol{e}_3 = \xi\boldsymbol{j} + \bar{\xi}\bar{\boldsymbol{j}} + z\boldsymbol{e}.$$

Replacing $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ by their expressions (46.2) and comparing coefficients of equal vectors, we find

$$\xi = x - iy, \quad \bar{\xi} = x + iy, \quad z = z. \tag{46.3}$$

Thus, here too, a bar is the symbol of complex conjugation.

Now let us rotate the coordinate system about the axis X_3 through the angle φ. The new Cartesian basic vectors are

$$\begin{aligned} \boldsymbol{e}_{1'} &= \boldsymbol{e}_1 \cos\varphi + \boldsymbol{e}_2 \sin\varphi, \\ \boldsymbol{e}_{2'} &= -\boldsymbol{e}_1 \sin\varphi + \boldsymbol{e}_2 \cos\varphi, \\ \boldsymbol{e}_{3'} &= \boldsymbol{e}_3. \end{aligned} \tag{46.4}$$

A new cyclic basis

$$\boldsymbol{j}' = \frac{1}{2}(\boldsymbol{e}_{1'} + i\boldsymbol{e}_{2'}), \quad \bar{\boldsymbol{j}}' = \frac{1}{2}(\boldsymbol{e}_{1'} - i\boldsymbol{e}_{2'}), \quad \boldsymbol{e}' = \boldsymbol{e}_{3'} \tag{46.5}$$

corresponds to them. To obtain the law of the transformation of cyclic basic vectors under such a rotation of the coordinate system we shall express the new mutually orthogonal unit vectors in terms of the old unit vectors and the latter, with the aid of (46.2), in terms of the old cyclic basic vectors. Then we obtain

$$\boldsymbol{j}' = e^{-i\varphi}\boldsymbol{j}, \quad \bar{\boldsymbol{j}}' = e^{i\varphi}\bar{\boldsymbol{j}}, \quad \boldsymbol{e}' = \boldsymbol{e}. \tag{46.6}$$

Hence we find the law of the transformation of components. Since

$$\xi\boldsymbol{j} + \bar{\xi}\bar{\boldsymbol{j}} + z\boldsymbol{e} = \bar{\xi}'\boldsymbol{j}' + \bar{\xi}'\bar{\boldsymbol{j}}' + z'\boldsymbol{e}',$$

it is evident that

$$\xi' = e^{i\varphi}\xi, \quad \bar{\xi}' = e^{-i\varphi}\bar{\xi}, \quad z' = z. \tag{46.7}$$

If the component ξ is given an index 1, the component $\bar{\xi}$ an index -1, and the component z an index 0, the law of the transformation of the cyclic components (but not of basic vectors!) under the rotation about the axis X_3 can be written down with the aid of matrix $\| c_{k'l} \|$

$$c_{k'l} = e^{ik'\varphi}\delta_{k'l} = e^{il\varphi}\delta_{k'l} \tag{46.8}$$

as

$$A_{k'} = c_{k'l}A_l = e^{il\varphi}\delta_{k'l}A_l. \tag{46.9}$$

Correspondingly, the law of the transformation of cyclic components of an r-rank tensor $\mathbf{A}$ under rotation through the angle φ about the axis X_3 can be expressed as

$$A_{k_1'\ldots k_r'} = \exp\left[i(l_1 + \ldots + l_r)\varphi\right]\delta_{k_1'l_1} \ldots \delta_{k_r'l_r}A_{l_1\ldots l_r}. \tag{46.10}$$

If the rotation about the axis X_3 is a unit turn about an N-fold symmetry axis, then $\varphi = 2\pi/N$ and

$$c_{k'l} = \exp\left(\frac{2\pi i}{N}\, l\right) \delta_{k'l}. \tag{46.11}$$

Now let us imagine that the r-rank tensor **A** is specified by its components $A_{l_1 \ldots l_r}$ with respect to the cyclic system of coordinates. Let us formulate the conditions which must be satisfied by these components so that tensor **A** would be invariant with respect to group N (i.e. with respect to rotations about the N-fold symmetry axis). We have written matrix $\| c_{k'l} \|$ in a form that is very convenient for substitution into the main equation of invariance (44.3). Having done this, we obtain

$$\left\{\exp\left[\frac{2\pi i}{N}(l_1 + \ldots + l_r)\right] - 1\right\} A_{l_1 \ldots l_r} = 0. \tag{46.12}$$

Only those components will differ from zero for which the expression in parentheses vanishes. But $e^{2\pi i s} = 1$ when, and only when, s is an integer or zero. Thus, only those cyclic components of a tensor invariant with respect to the group N differ from zero, the sum of whose indices is zero or is divisible by N. We have obtained a very simple convention which permits us to write out immediately all the non-zero components of the tensor invariant with respect to any group of rotations, although only in the cyclic system of coordinates. Let us list, for example, the non-zero cyclic components of a fourth-rank tensor **A** invariant with respect to group 3 (for convenience we write the minus sign over the index):

$$A_{\bar{1}\bar{1}\bar{1}\bar{0}},\quad A_{\bar{1}\bar{1}11},\quad A_{\bar{1}001},\quad A_{0000},\quad A_{0111},$$

as well as the components resulting from the above upon any permutation of indices (the total number of surviving components is $4 + 6 + 12 + 1 + 4 = 27$).

Let us see how these results change in case of inversion rotations. Under inversion the cyclic components behave in the same way as the Cartesian ones: they all reverse their signs. Therefore the matrix of the transformation of cyclic components under inversion rotation differs from the matrix earlier obtained for a simple rotation only in sign:

$$c_{k'l} = -e^{il\varphi} \delta_{k'l}. \tag{46.13}$$

The condition for the invariance of the tensor with respect to the N-fold inversion axis is therefore expressed as

$$\left\{(-1)^r \exp\left[\frac{2\pi i}{N}(l_1 + \ldots + l_r)\right] - 1\right\} A_{l_1 \ldots l_r} = 0, \tag{46.14}$$

where r is the rank of tensor **A**. Thus, for even-rank tensors it does not at all differ from the invariance condition with respect to a simple symmetry axis of the same order. In odd-rank tensors invariant with respect to the $\bar{N}$ group only those components are non-zero for which the quotient of the division of the sum of the indices by the order of the axis is a half-integer:

$$\frac{1}{N}(l_1 + \ldots + l_r) = \pm\frac{1}{2},\ \pm\frac{3}{2},\ \pm\frac{5}{2},\ \ldots \qquad (46.15)$$

Indeed under this and only under this condition the square brackets in the invariance equation (46.14) vanishes at an odd r.

There is no trouble in the generalization of the derived invariance conditions for pseudotensors.

If only those cyclic components of a tensor survive the sum of whose indices is zero, then the tensor is apparently invariant with respect to any group of rotations, because the invariance condition holds for it with any N. But this means that the given tensor is invariant with respect to the limit group ∞ and it is obvious that only such tensors have this property. This result not only gives the possibility of finding the general form of matter tensors for textures, but also allows proving one of the most important theorems of theoretical crystal physics.

Hermann's Theorem. If an r-rank tensor has an N-fold symmetry axis and $r < N$, then this tensor also has a symmetry axis of an infinite order (Hermann, 1934; 1945).

The proof of this theorem is very simple. Since cyclic indices take only values of -1, 0, 1, their absolute sum for any component will not exceed rank r of the tensor. If $r < N$, then for the invariance condition to hold it is necessary for this sum of non-zero components to be zero, this meaning that the tensor has a symmetry axis of an infinite order.

Hermann's theorem has numerous applications. According to this theorem second-rank matter tensors for the crystals of the intermediate category have an axis of an infinite order; we have already met with this fact when studying the dielectric properties of crystals. All the second-rank tensors for the cubic crystals are isotropic, because these crystals have four three-fold axes; this we have seen too. Next, third-rank tensors for crystals of classes 4 and 6 and for textures of class ∞ coincide in form; these tensors also coincide for crystals of classes 422, 622 and for textures of class $\infty 2$, for crystals of classes $4mm$, $6mm$ and for textures of class ∞m. Fourth-rank tensors coincide in form for the subsystems $6/m$ and ∞/m, as well as for the subsystems $6/mmm$ and ∞mm. The importance of these facts for crystal physics will be seen later, when we become acquainted with the properties described by the third- and fourth-rank tensors.

So, we know how to write out the surviving cyclic components of tensors invariant with respect to groups N and $\bar{N}$ and also invariant with respect to the limit group ∞. But we need the Cartesian components of tensors and not the cyclic ones. This calls for a convenient method of transforming the cyclic components into the Cartesian ones. We shall see that here also use can be made of the transformation of tensor components as of the products of corresponding coordinates; the method which we shall show in some examples below is based exactly on this fact.

Let us agree on notation. Instead of cyclic indices 1, 0 and —1, we shall write ξ, z and $\bar{\xi}$ respectively. Tensor components will be denoted by braces with coefficients, e.g. $a\,\{\xi\xi\xi\}$; the term enclosed in these braces showing what are the indices of a given component, and the coefficient showing to what the component is equal.

It is possible to perform identical transformations with the term in the braces, in accordance with formula (46.3), i.e.

$$\{\xi\} = \{x - iy\} = \{x\} - i\,\{y\},$$

$$\{\bar{\xi}\} = \{x + iy\} = \{x\} + i\,\{y\}.$$

If the braces enclose two or more indices, a multiplication is necessary; it is done in the usual manner, with a single complication: no rearrangement of the factors of the product can be made, since it would mean the permutation of indices. Coefficient i can be moved anywhere and even factored out from the braces. For example,

$$\{\xi\xi\} = \{(x - iy)\,(x - iy)\} = \{xx\} - \{yy\} - i\,\{xy\} - i\,\{yx\}.$$

The braces $\{\bar{\xi}\bar{\xi}\bar{\xi}\}$ are obtained directly from the preceding ones by means of complex conjugation, i.e. by changing the signs of the imaginary terms; this cuts the number of necessary calculations in two. Let us also note that having calculated, say, the braces

$$\{\xi\xi\bar{\xi}\} = \{xxx\} + \{xyy\} + \{yxy\} - \{yyx\} + \\ + i\,(\{xxy\} - \{xyx\} - \{yxx\} - \{yyy\}),$$

it is possible to write out immediately the braces $\{\xi\bar{\xi}\xi\}$ and $\{\bar{\xi}\xi\xi\}$ by simply making corresponding permutations also in the right-hand side of the equality: to obtain $\{\xi\bar{\xi}\xi\}$, it is necessary to interchange the places of the second and third indices in all braces of the right-hand side, and to obtain $\{\bar{\xi}\xi\xi\}$ to do the same with the first and third indices.

Let us discuss an example: we calculate a third-rank tensor invariant with respect to rotations about a three-fold axis. We write it out as

$$g = a\,\{\xi\xi\xi\} + \bar{a}\,\{\bar{\xi}\bar{\xi}\bar{\xi}\} + b_1\,\{\xi\xi z\} + b_1\,\{\bar{\xi}\bar{\xi}z\} + \\ + b_2\,\{\xi z\xi\} + \bar{b}_2\,\{\bar{\xi}z\bar{\xi}\} + b_3\,\{z\xi\xi\} + \bar{b}_3\,\{z\bar{\xi}\bar{\xi}\} + d\,\{zzz\}$$

All its non-vanishing components are given here; a, $\bar{a}$, b_1, $\bar{b}_1$, . . . are arbitrary complex coefficients. Upon removing the braces we obtain

$$g = (a+\bar{a})\,(\{xxx\}-\{xyy\}-\{yxy\}-\{yyx\})+$$
$$+\,i\,(a-\bar{a})\,(\{yyy\}-\{xxy\}-\{xyx\}-\{yxx\})+$$
$$+\,(b_1+\bar{b}_1)\,(\{xxz\}+\{yyz\})+i\,(b_1-\bar{b}_1)\,(\{xyz\}-$$
$$-\{yxz\})+(b_2+\bar{b}_2)\,(\{xzx\}+\{yzy\})+i\,(b-\bar{b}_2)\,\{xzy\}-$$
$$-\{yzx\})+(b_3+\bar{b}_3)\,\{zxx\}+\{zyy\})+i\,(b_3-\bar{b}_3)\,(\{zxy\}-$$
$$-\{zyx\})+d\,\{zzz\}.$$

Apparently, the coefficients preceding the braces composed of indices x, y, z are the corresponding components in Cartesian coordinates. If **g** is a matter tensor, then a and $\bar{a}$, b_1 and $\bar{b}_1$, etc. are complex-conjugate numbers, since they serve as coefficients of the complex-conjugate braces. Many of the components turned out to be connected between themselves. Indeed, the equality obtained means that the following components are non-zero

$$[xxx]=-[xyy]=-[yxy]=-[yyx] \quad \text{or} \quad g_{111}=-g_{122}=-g_{212}=-g_{221},$$
$$[yyy]=-[xxy]=-[xyx]=-[yxx] \quad \text{or} \quad g_{222}=-g_{112}=-g_{121}=-g_{211},$$
$$[xxz]=[yyz] \quad \text{or} \quad g_{113}=g_{223},$$
$$[xyz]=-[yxz[\quad \text{or} \quad g_{123}=-g_{213},$$
$$[xzx]=-[yzy] \quad \text{or} \quad g_{131}=-g_{232},$$
$$[xzy]=-[yzx] \quad \text{or} \quad g_{132}=-g_{231},$$
$$[zxx]=[zyy| \quad \text{or} \quad g_{311}=g_{322},$$
$$[zxy]=-[zyx] \quad \text{or} \quad g_{312}=-g_{321},$$
$$[zzz] \quad \text{or} \quad g_{333}.$$

Thus, of the 21 non-zero components there are only 9 independent ones.

Let us now consider tensor **d** which is also invariant with respect to group 3, but is, moreover, symmetric with respect to the second and third indices. Its non-zero components are:

$$d_{111}=-d_{122}=-d_{212}=-d_{221}, \qquad d_{222}=-d_{112}=-d_{121}=-d_{211},$$
$$d_{113}=d_{131}=d_{223}=d_{232}, \qquad d_{123}=d_{132}=-d_{213}=-d_{231},$$
$$d_{311}=d_{322},\ d_{333}.$$

There are 19 of them in all, and 6 are independent.

Finally, tensor **f** symmetric with respect to all indices and invariant with respect to the same group, has the following non-zero components:

$$f_{111}=-f_{122}=-f_{212}=-f_{221}, \qquad f_{222}=-f_{112}=-f_{121}=-f_{211},$$
$$f_{113}=f_{131}=f_{311}=f_{223}=f_{322}=f_{232}, \qquad f_{333}.$$

There are 15 of them, but only 4 are independent.

It is not difficult to construct corresponding tensors invariant with respect to group 32 or $3m$. It is only necessary to eliminate vanishing components because of the requirement of invariance with respect to 2_x or m_x respectively. Thus, with the aid of the table compiled out especially for a third-rank tensor in the preceding Section, we shall find the non-zero components of tensor **g** for

group 32:

$$g_{111} = -g_{122} = -g_{212} = -g_{221},$$

$$g_{123} = -g_{213}, \quad g_{132} = -g_{231}, \quad g_{312} = -g_{321}.$$

of tensor **d**:

$$d_{111} = -d_{122} = -d_{212} = -d_{221}, \quad d_{123} = d_{132} = -d_{213} = -d_{231}$$

and finally of tensor **f**:

$$f_{111} = -f_{122} = -f_{212} = -f_{221}.$$

For another method of constructing tensors invariant with respect to the groups of the trigonal and hexagonal systems see Fumi (1952a, b); Fieschi and Fumi (1953).

Sec. 47. Application of the Theory of Group Representation to the Problems of Tensor Symmetry

Many problems connected with the symmetry of tensors are solved with the aid of special mathematical methods that are based on the more profound results of the theory of groups (to be more exact—of one of its branches called the theory of the group representation). Lately these methods have been widely used in all branches of theoretical physics in which it is necessary to take account of the symmetry of objects under investigation: in the theory of molecular and crystal spectra, in the theory of elementary particles, in the theory of nuclear reactions, and so on.

Here we shall give only two results concerning the symmetry of tensors, without supplying their proofs. The first one is the method of constructing a tensor invariant with respect to a given crystallographic group G by averaging the tensor over the group: all symmetry operations g included in group G should be performed on the general tensor **A** with a specified internal symmetry and then the arithmetical mean must be computed over all the obtained results:

$$\langle \mathbf{A} \rangle_G = \frac{1}{N(G)} \sum_{g \in G} g\mathbf{A}. \tag{47.1}$$

If group G has two generators, it is more convenient to average the tensor first in respect of subgroup H_1 defined by one generator, and to average the result of this averaging over subgroup H_2 defined by another generator. The sequence of the successive averaging is of no importance. For instance, a tensor invariant with respect to group 422 (its generators are 4_z and 2_x) can be computed both in this way

$$\langle \mathbf{A} \rangle_4 = \frac{1}{4} (\mathbf{A} + 4_z\mathbf{A} + 2_z\mathbf{A} + 4_z^3\mathbf{A}),$$

$$\langle \mathbf{A} \rangle_{422} = \frac{1}{2} (\langle \mathbf{A} \rangle_4 + 2_x \langle \mathbf{A} \rangle_4),$$

and in the other way

$$\langle \mathbf{A} \rangle_2 = \frac{1}{2} (\mathbf{A} + 2_x \mathbf{A}),$$

$$\langle \mathbf{A} \rangle_{422} = \frac{1}{4} (\langle \mathbf{A} \rangle_2 + 4_z \langle \mathbf{A} \rangle_2 + 2_z \langle \mathbf{A} \rangle_2 + 4_z^3 \langle \mathbf{A}_2 \rangle).$$

The second important result obtained with the aid of the methods of the theory of group representation is that it is possible to compute the number of the independent components of a tensor with specified external and internal symmetries without computing the tensor itself (Bhagavantam and Suryanarayana, 1949; Jahn, 1949)*. This number is equal to the value of character χ_T of a corresponding tensor representation T averaged over the crystallographic** group G:

$$\langle \chi_T \rangle_G = \frac{1}{N(G)} \sum_{g \in G} \chi_T (g). \tag{47.2}$$

By this method there were found mistakes that have been once made in the computation of the tensors of piezooptical coefficients (see Section 77 and Table E.19) and were not noticed later by research workers for thirty-five years.

Table 47.1 gives the number of independent components of tensors and pseudotensors with different external and internal symmetries up to the eighth rank inclusive. Table 47.1*a* contains even-type tensors and pseudotensors, and Table 47.1*b* those of the odd type. In the first Table all the 39 crystallographic and limit groups are combined into subsystems, since the general form of an even-type tensor, invariant with respect to a crystallographic or limit group, is the same for all groups included in a subsystem. There are 14 such subsystems (11 crystallographic and 3 limit ones). The second Table has only non-centrosymmetric groups, since the tensor quantities of the odd type, invariant with respect to centrosymmetric groups, are identically zero. There are 25 non-centrosymmetric groups (21 crystallographic and 4 limit ones).

The tables show not only the number of the independent components of a tensor but also the number of its independent invariants when it differs from the former. In such cases to a subsystem in Table 47.1*a* or to a group in Table 47.1*b* there correspond two rows of numbers: the upper row shows the number of independent components, the lower row—the number of independent invariants.

The difference between the number of independent components and the number of independent invariants is equal to the number of

* See also Bhagavantam and Venkatarayudu (1962).

** This method can also be used for limit groups—then the averaging is done by integrating over a group.

parameters required for specifying the orientation of a given tensor with respect to a coordinate system. Thus, a vector has only one independent invariant—its length. In crystals with a symmetry axis a matter vector should coincide with it in direction. This requirement fully defines the orientation of the vector with respect to the coordinate system. Therefore the number of independent components of a vector, for these classes, is equal to the number of its independent invariants, i.e. to unity. In crystals of class m a matter vector lies in the symmetry plane, and one parameter is required to show its direction; therefore the number of independent components increases to two. Finally, in class 1 the vector direction is in no way restricted, and two parameters are required to specify it; correspondingly the number of independent components increases to three.

Another example is a symmetric second-rank tensor $[V^2]$. Its eigenvalues can be considered to be its independent invariants, since they fully define the shape and dimensions of the tensor's representation surface. In crystals of the higher category the representation surface is a sphere; it is characterized by a single invariant; its orientation, naturally, need not be specified. In crystals of the intermediate category the representation surface is one of revolution and is specified by two invariants. For its orientation it would suffice to show the direction of the axis of rotation, but it coincides with the principal symmetry axis of the crystal, and therefore in this case too the number of independent components is equal to the number of independent invariants—it is two. In crystals of the lower category the representation surface is characterized by three independent invariants. For specifying its orientation it is enough to show the location of its symmetry axes. In crystals of the orthorhombic system they coincide with the crystals symmetry axes, so that no additional parameters are required for the orientation of the representation surface. In crystals of the monoclinic system there is needed an additional parameter characterizing the rotation of the representation surface about a two-fold axis or a perpendicular to the symmetry plane of the crystal, so that the number of independent components increases to four. In crystals of the triclinic system three additional parameters are necessary for the orientation of the representation surface with respect to the coordinate system, and the number of independent components is six.

Table 47.1 permits drawing some conclusions on the form of tensors invariant with respect to the specified groups, as well as on the symmetry of tensors and tensor-functions.

If two tensors with different internal symmetries which are invariant with respect to the same crystallographic or limit group, have the same number of independent components, and one of their internal symmetry groups is a subgroup of another group, then the

Table 47.1a

The Number of Independent Components and Independent Invariants of Even-Type Tensors

Point groups	$D_0 \sim \varepsilon\{V^3\}$	$\varepsilon V \sim \varepsilon D_1 \sim \{V^2\}$	D_2	$[V^2]$	V^2	εD_3	$\varepsilon[V^3]$	$\varepsilon V[V^2] \sim [V^2]\{V^2\}$	εV^3	D_4	$[V^4]$	$V[V^3]$	$[[V^2]^2]$
$\infty\infty m$, $\infty\infty$	1	0	0	1	1	0	0	0	1	0	1	1	2
$m3m$, 432, $\bar{4}3m$	1	0	0	1	1	0	0	0	1	1	2	2	3
$m3$, 23	1	0	0	1	1	1	1	1	2	1	2	3	3
∞/mm, ∞m, $\infty 2$	1	0	1	2	2	0	0	1	3	1	3	4	5
∞/m, ∞	1	1	1	2	3	1	2	4	7	1	3	6	5
$6/mmm$, 622, $6mm$, $\bar{6}m2$	1	0	1	2	2	0	0	1	3	1	3	4	5
$6/m$, 6, $\bar{6}$	1	1	1	2	3	1	2	4	7	1	3	6	5
$4/mmm$, 422, $4mm$, $\bar{4}2m$	1	0	1	2	2	0	0	1	3	2	4	5	6
										3	5	8	7
$4/m$, 4, $\bar{4}$	1	1	1	2	3	1	2	4	7				
										2	4	7	6
$\bar{3}m$, 32, $3m$	1	0	1	2	2	1	1	2	4	2	4	6	6
						3	4	6	9	3	5	10	7
$\bar{3}$, 3	1	1	1	2	3								
						2	3	5	8	2	4	9	6
mmm, 222, $mm2$	1	0	2	3	3	1	1	3	6	3	6	9	9
			3	4	5	3	4	8	13	5	9	16	13
$2/m$, 2, m	1	1											
			2	3	4	2	3	7	12	4	8	15	12
		3	5	6	9	7	10	18	27	9	15	30	21
$\bar{1}$, 1	1												
		1	2	3	6	4	7	15	24	6	12	27	18

Table 47.1a (cont'd)

Point groups	$[V^2]^2$	$[(V^2)^2]$	$V^2[V^2]$	V^4	εD_6	$\varepsilon[V^3]$	$\varepsilon V[V^4]$	$\varepsilon[V^2][V^3]$	$\varepsilon V[[V^2]^2]$	$\varepsilon V^2[V^3]$	$\varepsilon V[V^2]^2$	$\varepsilon V^3[V^2]$
$\infty\infty m$, $\infty\infty$	2	3	2	3	0	0	0	0	0	1	1	3
$m3m$, 432, $\bar{4}3m$	3	4	3	4	0	0	1	1	1	3	3	6
$m3$, 23	4	5	5	7	0	1	3	4	4	7	8	13
∞/mm, ∞m, $\infty 2$	6	8	7	10	0	0	2	3	3	7	8	15
∞/m, ∞	8	11	12	19	1	3	7	10	11	16	20	32
$6/mmm$, 622, $6mm$, $\bar{6}m2$	6	8	7	10	0	0	2	3	3	7	8	15
$6/m$, 6, $\bar{6}$	8	11	12	19	1	3	7	10	11	16	20	32
$4/mmm$, 422, $4mm$, $\bar{4}2m$	7	9	8	11	1	1	4	5	5	10	11	19
$4/m$, 4, 4	10	13	14	21	3	5	11	14	15	22	26	40
	9	12	13	20	2	4	10	13	14	21	25	39
$\bar{3}m$, 32, $3m$	8	10	10	14	1	2	6	8	8	14	16	26
$\bar{3}$, 3	12	15	18	27	3	7	15	20	21	30	36	54
	11	14	17	26	2	6	14	19	20	29	35	53
mmm, 222, $mm2$	12	15	15	21	2	3	9	12	12	21	24	39
$2/m$, 2, m	20	25	28	41	5	9	21	28	29	44	52	80
	19	24	27	40	4	8	20	27	28	43	51	79
$\bar{1}$, 1	36	45	54	81	11	21	45	60	63	90	108	162
	33	42	51	78	8	18	42	57	60	87	105	159

Table 47.1a (cont'd)

Point groups	D_6	$[V^6]$	$V\,[V^5]$	$[[V^2]^3]$	$[V^2]\,[V^4]$	$[V^2]\,[[V^2]^2]$	$[V^2]^3$	εD_7	$\varepsilon\,[V^7]$	$\varepsilon V\,[V^6]$	D_∞	$[V^8]$	$V\,[V^7]$	$[V^2]\,[V^6]$
$\infty\ \infty m$, $\infty\ \infty$	0	1	1	3	2	4	5	0	0	0	0	1	1	2
$m3m$, 432, $\bar{4}3m$	1	3	4	6	6	9	12	0	0	2	1	4	6	10
$m3$, 23	2	4	6	8	9	13	20	1	2	6	1	5	10	16
∞/mm, ∞m, $\infty 2$	1	4	6	9	10	16	23	0	0	3	1	5	8	14
∞/m, ∞	1	4	9	10	14	22	38	1	4	10	1	5	12	20
$6/mmm$, 622, $6mm$, $\bar{6}m2$	2	5	7	10	11	17	24	1	1	5	2	7	12	19
$6/m$, 6, $\bar{6}$	3	6	11	12	16	24	40	3	6	14	3	9	20	30
	2	5	10	11	15	23	39	2	5	13	2	8	19	29
$4/mmm$, 422, $4mm$, $\bar{4}2m$	2	6	10	12	15	22	32	1	2	8	3	9	16	26
$4/m$, 4, $\bar{4}$	3	8	17	16	24	34	56	3	8	20	5	13	28	44
	2	7	16	15	23	33	55	2	7	19	4	12	27	43
$\bar{3}m$, 32, $3m$	3	7	12	14	18	26	40	2	4	12	3	10	20	32
$\bar{3}$, 3	5	10	21	20	30	42	72	5	12	28	5	15	36	56
	4	9	20	19	29	41	71	4	11	27	4	14	35	55
mmm, 222, $mm2$	4	10	18	20	27	39	60	3	6	18	5	15	30	48
$2/m$, 2, m	7	16	33	32	48	68	112	7	16	40	9	25	56	88
	6	15	32	31	47	67	111	6	15	39	8	24	55	87
$\bar{1}$, 1	13	28	63	56	90	126	216	15	36	84	17	45	108	168
	10	25	60	53	87	123	213	12	33	81	14	42	105	165

The Number of Independent Components and Independent Invariants of Odd-type Tensors

Point groups	$\varepsilon=\varepsilon D_0=\{\varepsilon V^3\}$	$D_1=V=\varepsilon\{\varepsilon V^2\}$	εD_2	$\varepsilon[V^2]\varepsilon$	$\varepsilon V^2=V\{\varepsilon V^2\}$	D_3	$[\varepsilon V^3]$	$V[\varepsilon V^2]V$	εV^3	εD_4	$\varepsilon[V^4]\varepsilon$	$\varepsilon V[V^3]=\{\varepsilon V^2\}[V^3]$	$\varepsilon[\varepsilon V^2]^2\varepsilon$	$\varepsilon[V^2]^2\varepsilon$	D_5	$[V^5]$	$V[V^4]V$	$V[V^2]^2V$	$[\varepsilon V^2][\varepsilon V^2]$	$V^2[\varepsilon V^2]$	$V[\varepsilon V^2]^2V$	$V^3[\varepsilon V^2]$	D_7	$[V^7]$	$V[\varepsilon V^6]V$
$\infty\infty$	1	0	0	1	1	0	0	0	1	0	1	1	2	2	0	0	0	0	0	1	1	3	0	0	0
432	1	0	0	1	1	0	0	0	1	1	2	2	3	3	0	0	1	1	1	3	3	6	0	0	2
$\bar{4}3m$	0	0	0	0	0	1	1	1	1	0	0	1	0	1	0	1	2	3	3	4	5	7	1	2	4
23	1	0	0	1	1	1	1	1	2	1	2	3	3	4	0	1	3	4	4	7	8	13	1	2	6
$\infty 2$	1	0	1	2	2	0	0	1	3	1	3	4	5	6	0	0	2	3	3	7	8	15	0	0	3
∞m	0	1	0	0	1	1	2	3	4	0	0	2	0	2	1	3	5	8	7	9	12	17	1	4	7
∞	1	1	1	2	3	1	2	4	7	1	3	6	5	8	1	3	7	11	10	16	20	32	1	4	10
622	1	0	1	2	2	0	0	1	3	1	3	4	5	6	0	0	2	3	3	7	8	15	1	1	5
$6mm$	0	1	0	0	1	1	2	3	4	0	0	2	0	2	1	3	5	8	7	9	12	17	2	5	9
$\bar{6}m2$	0	0	0	0	0	1	1	1	1	1	1	2	1	2	1	2	4	5	5	7	8	11	1	3	7
6	1	1	1	2	3	1	2	4	7	1	3	6	5	8	1	3	7	11	10	16	20	32	3	6	14
																							2	5	13
$\bar{6}$	0	0	0	0	0	2	2	2	2	2	2	4	2	4	2	4	8	10	10	14	16	22	2	6	14
						1	1	1	1	1	1	3	1	3	1	3	7	9	9	13	15	21	1	5	13

Table 47.1b (cont'd)

Point groups	$\varepsilon=\varepsilon D_0=\{V^3\}$	$D_1=V=\varepsilon\{V^2\}$	εD_2	$\varepsilon[V^2]$	$\varepsilon V^2=V\{V^2\}$	D_3	$[V^3]$	$V[V^2]$	V^3	εD_4	$\varepsilon[V^4]$	$\varepsilon V[V^3]=\{V^2\}[V^3]$	$\varepsilon[[V^2]^2]$	$\varepsilon[V^2]^2$	D_5	$[V^5]$	$V[V^4]$	$V[[V^2]^2]$	$[V^2][V^3]$	$V^2[V^3]$	$V[V^2]^2$	$V^3[V^2]$	D_7	$[V^7]$	$V[V^6]$
422	1	0	1	2	2	0	0	1	3	2	4	5	6	7	1	1	4	5	5	10	11	19	1	2	8
4*mm*	0	1	0	0	1	1	2	3	4	1	1	3	1	3	2	4	7	10	9	12	15	21	2	6	12
42*m*	0	0	1	1	1	1	1	2	3	1	2	4	3	5	1	2	5	7	7	11	13	20	2	4	10
										3	5	8	7	10	3	5	11	15	14	22	26	40	3	8	20
4	1	1	1	2	3	1	2	4	7																
										2	4	7	6	9	2	4	10	14	13	21	25	39	2	7	19
			2	2	2	2	2	4	6	2	4	8	6	10	2	4	10	14	14	22	26	40	4	8	20
$\bar{4}$	0	0																							
			1	1	1	1	1	3	5	1	3	7	5	9	1	3	9	13	13	21	25	39	3	7	19
32	1	0	1	2	2	1	1	2	4	2	4	6	6	8	1	2	6	8	8	14	16	26	2	4	12
3*m*	0	1	0	0	1	2	3	4	5	1	1	4	1	4	2	5	9	13	12	16	20	28	3	8	16
						3	4	6	9	3	5	10	7	12	3	7	15	21	20	30	36	54	5	12	28
3	1	1	1	2	3																				
						2	3	5	8	2	4	9	6	11	2	6	14	20	19	29	35	53	4	11	27
222	1	0	2	3	3	1	1	3	6	3	6	9	9	12	2	3	9	12	12	21	24	39	3	6	18
*mm*2	0	1	1	1	2	2	3	5	7	2	3	7	4	8	3	6	12	17	16	23	28	41	4	10	22
			3	4	5	3	4	8	13	5	9	16	13	20	5	9	21	29	28	44	52	80	7	16	40
2	1	1																							
			2	3	4	2	3	7	12	4	8	15	12	19	4	8	20	28	27	43	51	79	6	15	39
		2	2	2	4	4	6	10	14	4	6	14	8	16	6	12	24	34	32	46	56	82	8	20	44
m	0																								
		1	1	1	3	3	5	9	13	3	5	13	7	15	5	11	23	33	31	45	55	81	7	19	43
		3	5	6	9	7	10	18	27	9	15	30	21	36	11	21	45	63	60	90	108	162	15	36	84
1	1																								
		1	2	3	6	4	7	15	24	6	12	27	18	33	8	18	42	60	57	87	105	159	12	33	81

general form of these tensors is the same. Such are, e.g., tensors V^2 and $[V^2]$ invariant with respect to group *mmm*. If a second-rank tensor is invariant with respect to this group, it is always symmetric in indices. Table E.6 confirms this.

If the number of independent components of tensors of a given internal symmetry, invariant with respect to two groups, is the same and one of the groups is a subgroup of the other, the general form of these tensors is the same. In this case the symmetry of the tensors and of tensor-functions is naturally the same.

If the number of independent invariants in matter tensors of any two groups is the same, and one of the groups is a subgroup of the other, the external symmetry groups of these tensors coincide. If in this case the tensors have different numbers of independent components, the external symmetry groups of tensor-functions are also different. Thus, the number of independent invariants is connected with tensor symmetry, and the number of independent components with tensor-function symmetry. Thus, the coincidence of the number of independent invariants of tensor $[V^2]$ for the rhombic, monoclinic and triclinic systems shows that the external symmetry of this tensor is *mmm*, the same for all the three systems. On the contrary, the external symmetry of tensor function $[V^2]$ for these three systems is different, and is respectively *mmm*, $2/m$ and 1. The coincidence of the number of independent invariants of tensor $[[V^2]^2]$ for the higher and lower subsystems of the tetragonal system shows that the external symmetry of this tensor for the two subsystems is $4/mmm$. The symmetry of tensor-function $[[V^2]^2]$ for the lower and higher subsystems is different, since the number of their independent components is different.

Other examples can be cited when the computation of the number of independent components and the number of independent invariants show that the groups of the external symmetry of a tensor and a corresponding tensor-function do not coincide. Some cases of the non-coincidence of the symmetry groups of a tensor and tensor-function are given in Table 47.2.

In Table 47.1 symbols D_r denote *irreducible tensors* of rank r— these are tensors symmetric in all indices, with all their traces being zero. Thus, D_2 is the symbol of a symmetric second-rank tensor **T** whose trace $T_{ii} = 0$; D_3 is the symbol of a third-rank tensor symmetric in all indices and satisfying conditions $T_{ijj} = T_{jij} = T_{jji} = 0$. They are called irreducible because they are transformed according to the irreducible representation of the rotation group*. The irreducible tensors of the first four ranks have special names: *vector*, *deviator*, *septor*, *nonor* (Shouten, 1951).

* Spherical functions transform according to the same representations. For their connection with irreducible tensors see Shcherbakov (1972).

Table 47.2

Gases when the Tensor-Function Symmetry is Less than the Tensor Symmetry

S	G	m	G^{ω}	n
V	∞m	1	1	3
			m	2
εV	∞/m	1	$\bar{1}$	3
$[V^2]$	mmm	3	$\bar{1}$	6
			$2/m$	4
$\varepsilon\,[V^2]$	222	3	1	6
			2	4
	$\bar{4}2m$	1	m	2
			$\bar{4}$	2
$[V^3]$	$mm2$	3	2	4
	$3m$	3	3	4
	$\bar{4}3m$	1	$\bar{4}$	2
	$\bar{6}m2$	1	$\bar{6}$	2
$V\,[V^2]$	$\bar{6}m2$	1	$\bar{6}$	2

S	G	m	G^{ω}	n
V^3	$\bar{6}m2$	1	$\bar{6}$	2
$[V^4]$	$\bar{3}m$	4	$\bar{3}$	5
	$4/mmm$	4	$4/m$	5
$\varepsilon\,[V^4]$	32	4	3	5
	422	4	4	5
	$\bar{6}m2$	1	$\bar{6}$	2
$[[V^2]^2]$	$3m$	6	$\bar{3}$	7
	$4/mmm$	6	$4/m$	7
$\varepsilon\,[[V^2]^2]$	32	6	3	7
	422	6	4	7
	$\bar{6}m2$	1	$\bar{6}$	2
$[V^5]$	$4mm$	4	4	5
$[V^6]$	$6/mmm$	5	$6/m$	6
$[V^7]$	$6mm$	5	6	6

Notation. G and G^{ω} are the external symmetry groups of the tensor and tensor-function, S is their internal symmetry group, m and n are the numbers of the independent invariants and components respectively.

Table 47.3

Irreducible Tensors of Different Symmetries

Deviators and pseudodeviators

D **D**

	1	2	3		
	$-a$	0	0	1	222
mmm		$-b$	0	2	
			$a+b$	3	$2 \parallel X_1, X_2, X_3$

mmm	$-a$	0	0	$42m$
		a	0	
$4/mmm$			0	$4 \parallel X_3,\ 2 \parallel X_1$

∞/mm	$-a$	0	0	$\infty 2$
		$-a$	0	
			$2a$	$\infty \parallel X_3$

Septors and pseudoseptors

S **$\tilde{S}$**

	11	22	33	23	
1	$a+b$	$-a$	$-b$	g	
1 2	$-c$	$c+d$	$-d$		$\bar{1}$
3	$-e$	$-f$	$e+f$		

m	$a+b$	$-a$	$-b$	0	$\bar{1}$
	0	0	0		
$m \parallel X_2$	$-e$	$-f$	$e+f$		$2'/m'$

$mm2$	0	0	0	0	$2/m$
	0	0	0		
$2 \parallel X_3,\ m \perp X_1$	$-e$	$-f$	$e+f$		$2/mm'm'$

$3m$	0	0	0	0	$\bar{3}$
	$-c$	c	0		
$3 \parallel X_3,\ m \perp X_1$	$-e$	$-e$	$2e$		$\bar{3}m'$

$\bar{6}m2$	0	0	0	0	$\bar{3}m$
	$-c$	c	0		
$\bar{6} \parallel X_3,\ m \perp X_1$	0	0	0		$6'/mmm$

∞m	0	0	0	0	∞/m
	0	0	0		
$\infty \parallel X_3$	$-e$	$-e$	$2e$		∞/mm'

$43m$	0	0	0	g	$m3$
	0	0	0		
$4 \parallel X_1,\ X_2,\ X_3$	0	0	0		$m3m'$

Nonors and pseudononors

N **$\tilde{N}$**

	11	22	33	23	13	12	
	$b+c$	$-c$	$-b$	$d+e$	$-g$	$-h$	11
$\bar{1}$		$c+a$	$-a$	$-d$	$f+g$	$-k$	22 $\bar{1}$
			$a+b$	$-e$	$-f$	$h+k$	33

	$b+c$	$-c$	$-b$	0	$-g$	0	2
$2/m$		$c+a$	$-a$	0	$f+g$	0	
			$a+b$	0	$-f$	0	$2 \parallel X$

$\bar{1}$	0	0	0	$d+e$	0	$-h$	m
$2'/m'$		0	0	$-d$	0	$-k$	
			0	$-e$	0	$h+k$	$m \perp X_2$

Table 47.3 (cont'd)

mmm	$\begin{vmatrix} b+c & -c & -b & 0 & 0 & 0 \\ & c+a & -a & 0 & 0 & 0 \\ & & a+b & 0 & 0 & 0 \end{vmatrix}$	222	$2 \parallel X_1, X_2, X_3$
$2/m$	$\begin{vmatrix} 0 & 0 & 0 & 0 & 0 & -h \\ & 0 & 0 & 0 & 0 & -k \\ & & 0 & 0 & 0 & h+k \end{vmatrix}$	2	
$2/mm'm'$			$2 \parallel X_3,\ m \perp X_1$
$\bar{3}m$	$\begin{vmatrix} -3c & -c & 4c & d & 0 & 0 \\ & -3c & 4c & -d & 0 & 0 \\ & & -8c & 0 & 0 & 0 \end{vmatrix}$	32	$3 \parallel X_3,\ 2 \parallel X_1$
$4/mmm$	$\begin{vmatrix} a+c & -c & -a & 0 & 0 & 0 \\ & a+c & -a & 0 & 0 & 0 \\ & & 2a & 0 & 0 & 0 \end{vmatrix}$	422	$4 \parallel X_3,\ 2 \parallel X_1$
$4/mmm$	$\begin{vmatrix} 0 & 0 & 0 & 0 & 0 & -h \\ & 0 & 0 & 0 & 0 & h \\ & & 0 & 0 & 0 & 0 \end{vmatrix}$	$4mm$	
$8'/mm'm$			$4 \parallel X_3,\ m \perp X_1$
mmm	$\begin{vmatrix} -a & 0 & a & 0 & 0 & 0 \\ & a & -a & 0 & 0 & 0 \\ & & 0 & 0 & 0 & 0 \end{vmatrix}$	$\bar{4}2m$	
$4'/mmm'$			$\bar{4} \parallel X_3,\ 2 \parallel X_1$
$\bar{3}m$	$\begin{vmatrix} 0 & 0 & 0 & 0 & -g & 0 \\ & 0 & 0 & 0 & g & 0 \\ & & 0 & 0 & 0 & 0 \end{vmatrix}$	$\bar{6}m2$	
$6'/m'm'm$			$\bar{6} \parallel X_3,\ m \perp X_1$
∞/mm	$\begin{vmatrix} -3c & -c & 4c & 0 & 0 & 0 \\ & -3c & 4c & 0 & 0 & 0 \\ & & -8c & 0 & 0 & 0 \end{vmatrix}$	$\infty 2$	$\infty \parallel X_3$
$m3m$	$\begin{vmatrix} 2a & -a & -a & 0 & 0 & 0 \\ & 2a & -a & 0 & 0 & 0 \\ & & 2a & 0 & 0 & 0 \end{vmatrix}$	432	$4 \parallel X_1, X_2, X_3$

Table 47.3 gives these irreducible tensors of the odd type, differing in external symmetry (Sirotin, 1974). Tensors of the even type have the same form for each subsystem as the odd-type tensors have for the enantiomorphous class of the same subsystem, this having been used in the Table. To the odd-type tensors for non-enantiomorphous classes there correspond the even-type tensors that differ from the other tensors of the same subsystem by the antisymmetry group; this is also noted in Table 47.3 (see Secs. 67, 68 for the antisymmetry of tensors).

Many of the tensors listed in Table 47.3 have only one independent invariant; such are, for instance, the deviators of the ∞/mm symmetry, pseudodeviators $\infty 2$ and $\bar{4}2m$, septors $\bar{4}3m$, ∞m, $\bar{6}m2$. The representation surface of each such tensor has a quite definite shape, only its dimensions can differ depending on the magnitude of the

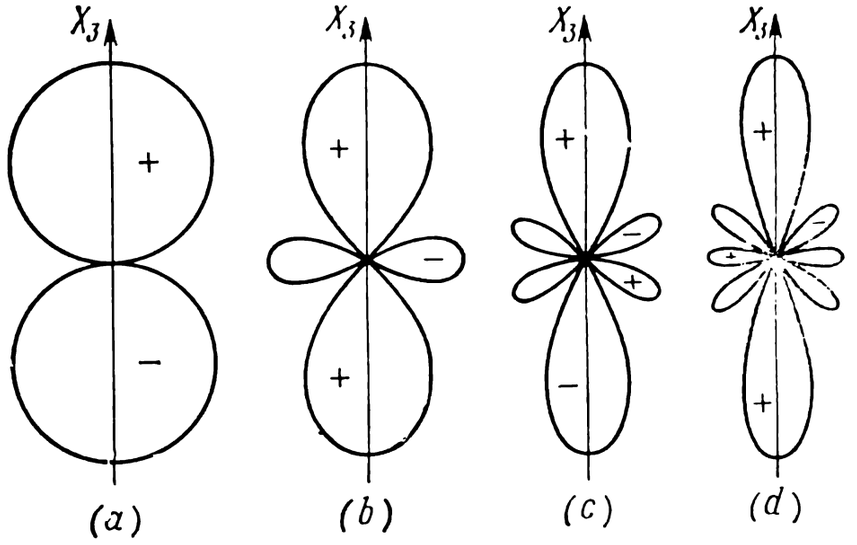


Fig. 47.1. Sections of the representation surfaces of unit tensors of: (a) vector $\mathbf{V}^0$ $[\infty m]$ and pseudotensor $\widetilde{\mathbf{V}}^0$ $[\infty/m]$, (b) deviator $\mathbf{D}^0$ $[\infty/mm]$ and pseudodeviator $\widetilde{\mathbf{D}}^0$ $[\infty 2]$, (c) septor $\mathbf{S}^0$ $[\infty m]$ and pseudoseptor $\widetilde{\mathbf{S}}^0$ $[\infty/m]$, (d) nonor $\mathbf{N}^0$ $[\infty/mm]$ and pseudononor $\widetilde{\mathbf{N}}^0$ $[\infty 2]$. In pseudotensors the positive and negative parts are replaced by the right- and left-hand ones (Butabayev and Sirotin, 1972)

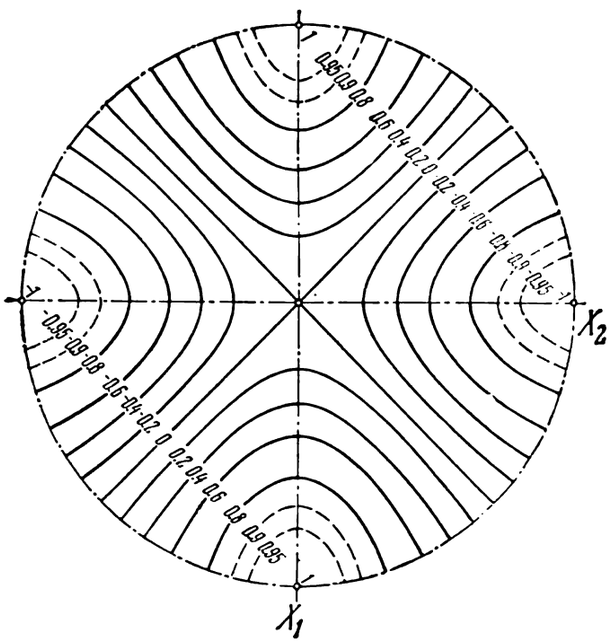


Fig. 47.2. Stereographic projection of the representation surface of a unit pseudotensor $\widetilde{\mathbf{D}}^0$ $[\bar{4}2m]$; positive numbers correspond to the right-hand sides, negative numbers to the left-hand sides. In stereographic projection the appearance of the representation surface of a unit deviator with symmetry mmm and antisymmetry $4'/m'mm'$ (see Sec. 68), is the same

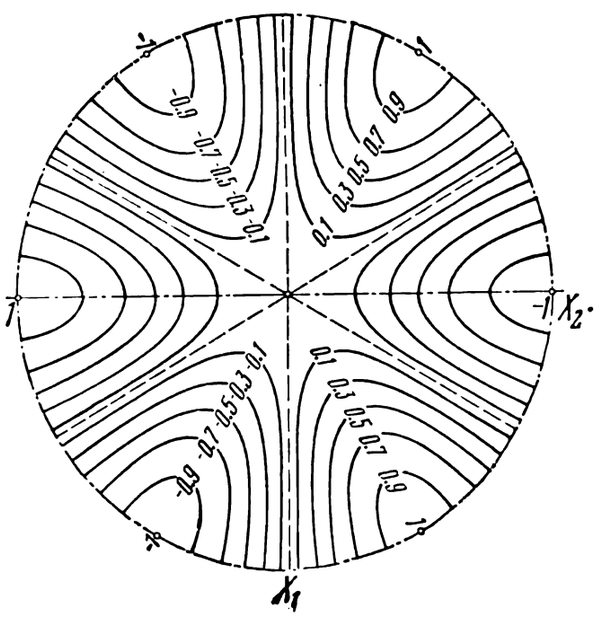


Fig. 47.3. Stereographic projection of the representation surface of a unit septor $\mathbf{S}^0$ $[\bar{6}m2]$ and pseudoseptor $\widetilde{\mathbf{S}}^0$ $[3m]$

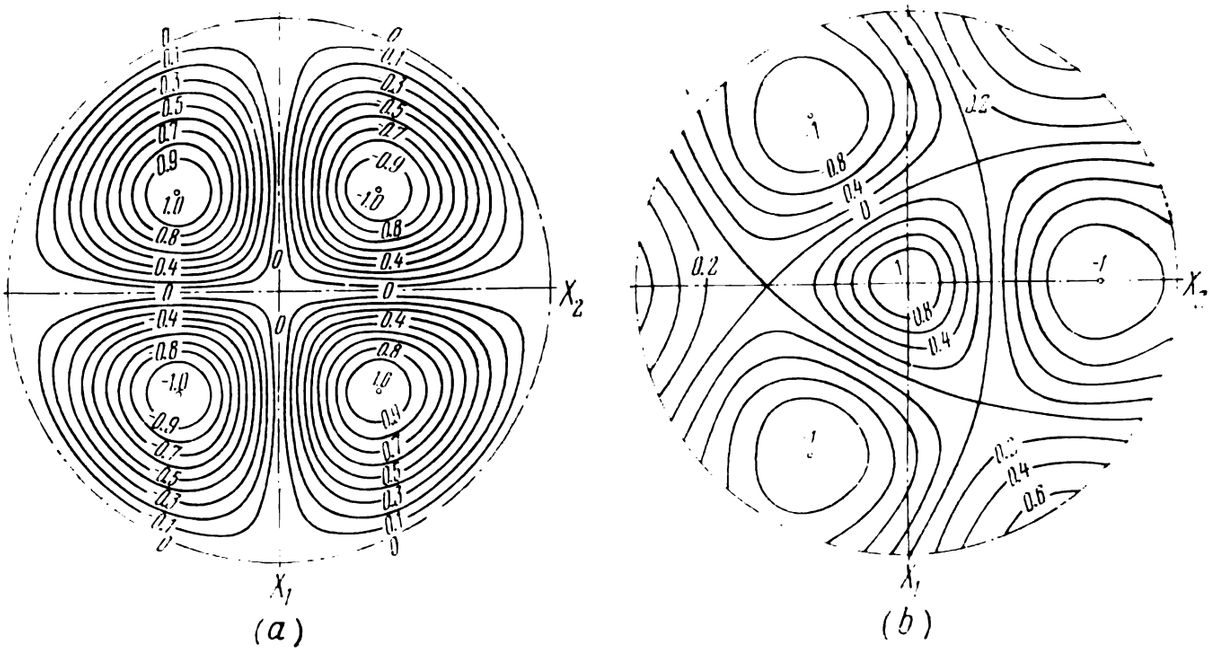


Fig. 47.4. Stereographic projections of the representation surface of a unit septor S^0 [$\bar{4}3m$] and pseudoseptor $\widetilde{S}^0[m^3]$: (a) in standard ("cubic") orientation $\bar{4} \parallel X_1, X_2, X_3$; (b) in "rhombohedral" orientation $3 \parallel X_3$, $m \perp X_1$

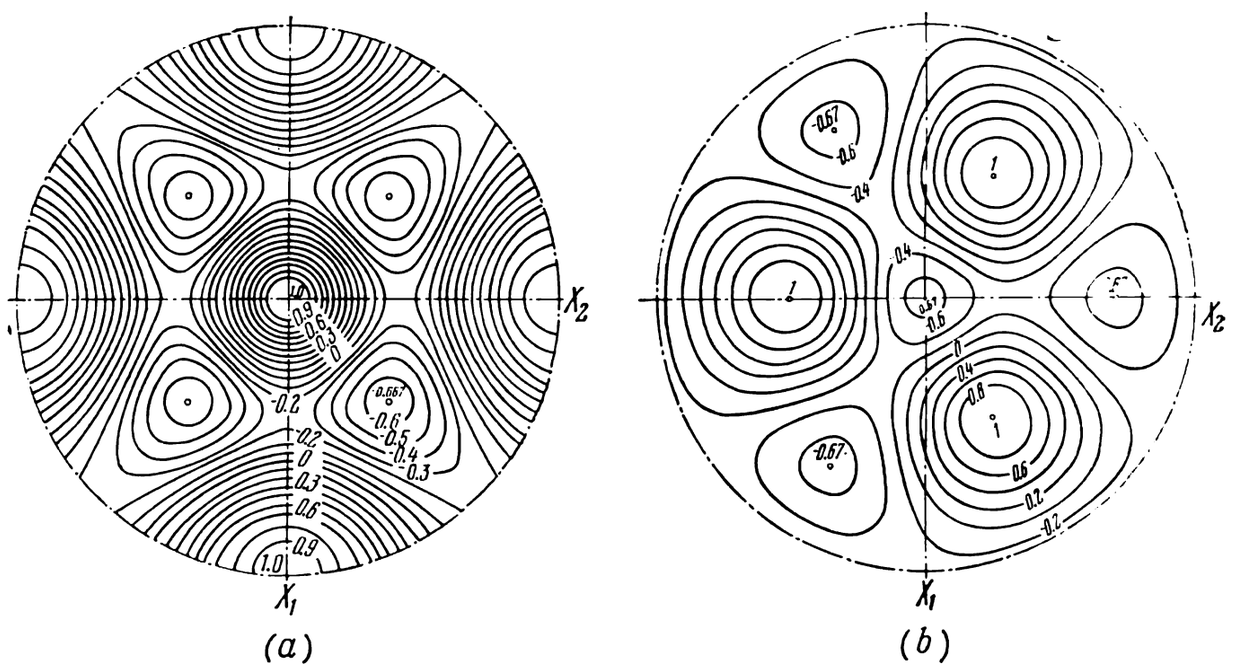


Fig. 47.5. Stereographic projections of the representation surface of a unit nonor N^0 [$m3m$] and pseudononor $\widetilde{N}^0$ [432]: (a) in standard ("cubic") orientation $4 \parallel X_1, X_2, X_3$; (b) in "rhombohedral" orientation $3 \parallel X_3$, $2 \parallel X_1$

invariant. If such a surface is within the sphere of a unit radius and contacts the sphere by its positive (or correspondingly the right-hand) part, we shall call it and the tensor that it represents the *unit* ones. Fig. 47.1 shows the sections of the representation surfaces of unit tensors and pseudotensors which possess an ∞ axis, and Figs. 47.2-47.6 show the projections of the representation surfaces of other unit tensors and pseudotensors (Butabayev and Sirotin, 1975). The non-zero components of these tensors and the equations of their representation surfaces are given in Table 47.4. It should be mentioned that the equations of the representation surfaces of irreducible unit tensors D_l with the axis ∞ are expressed by Legendre's polynomial P_l of l degree (see Jahnke, Emde, Lesch, 1933): $r=P_l(\cos\vartheta)$. The symmetry and antisymmetry of the irreducible unit tensors, the extremums of their normal components, as well as the isotropic planes can be well seen in the representation surfaces. In stereographic projections they appear as contour lines which coincide with great circles (in particular, with the circle of projection when the axis of isotropy is in the centre of projection, or with the diameter when the isotropy axis reaches the circumference of projection). Thus, Fig. 47.5 shows that for $\mathbf{N}^0$ $[m3m]$ the isotropic planes are $\{111\}$ (in Fig. 47.5*b* one of them reaches the circle of projection); in these planes $r = -0.25$.

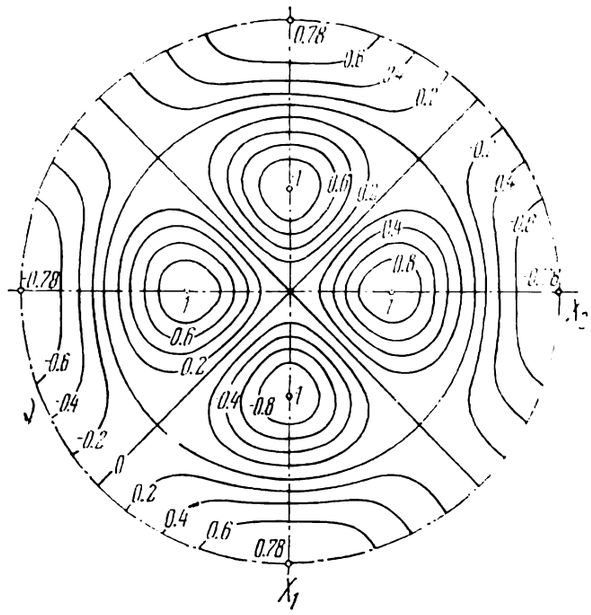


Fig. 47.6. Stereographic projection of the representation surface of a unit pseudononor $\widetilde{\mathbf{N}}^0$ $[\bar{4}2m]$; positive numbers correspond to the right-hand sides, negative numbers to the left-hand sides

For the other applications of the theory of group representation in crystal physics, especially in the theory of phase transitions and in the theory of the vibrations of a crystal (and the absorption spectra and combination scattering caused by them) see Bhagavantam and Venkatarayudu (1962); Wigner (1961); Heine (1963); Landau, Lifshitz (1974, 1976); Sushchinsky (1969); Knox, Gold (1970); Streitwolff (1971); Bhagavantam (1966).

Sec. 48. The Isotropic and Gyrotropic Tensors

The tensors invariant with respect to the group $\infty\infty m$ are called *isotropic*, and those invariant with respect to the group $\infty\infty$ are called *gyrotropic*. It is clear that only such tensors can describe the

Table 47.4

Irreducible Unit Tensors and Their Representation Surfaces

Tensors and their orientation	Zero components	Representation surface equation
$\mathbf{V}^0\,[\infty m]$, $\tilde{\mathbf{V}}^0\,[\infty/m]$, $\infty \parallel X_3$	$V^0_3 = 1$	$r = \cos\vartheta$
$\mathbf{D}^0\,[\infty/mm]$, $\tilde{\mathbf{D}}^0\,[\infty 2]$, $\infty \parallel X_3$	$D^0_{11} = D^0_{22} = -1/2$, $D^0_{33} = 1$	$r = (1/4)\,(1 + 3\cos 2\vartheta)$
$\tilde{\mathbf{D}}^0\,[\bar{4}2m]$, $\bar{4} \parallel X_3$, $2 \parallel X_1$	$D^0_{11} = 1$, $D^0_{22} = -1$	$r = (1/2)\,(1 - \cos 2\vartheta)\cos 2\varphi$
$\mathbf{S}^0\,[\infty m]$, $\tilde{\mathbf{S}}^0\,[\infty/m]$, $\infty \parallel X_3$	$S^0_{333} = 1$, $S^0_{113} = S^0_{223} = -1/2$	$r = (1/8)\,(3\cos\vartheta + 5\cos 3\vartheta)$
$\mathbf{S}^0\,[\bar{1}3m]$, $\tilde{\mathbf{S}}^0\,[m3]$, $2 \parallel X_1, X_2, X_3$	$S^0_{123} = \sqrt{3}/2$	$r = (3\sqrt{3}/8)\,(\cos\vartheta - \cos 3\vartheta)\sin 2\varphi$
$\mathbf{S}^0\,[\bar{4}3m]$, $\tilde{\mathbf{S}}^0\,[m3]$, $3 \parallel X_3$, $2 \parallel X_1$	$S^0_{333} = 1$, $S^0_{113} = S^0_{223} = -1/2$, $S^0_{112} = 1/\sqrt{2}$, $S^0_{222} = -1/\sqrt{2}$	$r = (1/8)\,[3\cos\vartheta + 5\cos 3\vartheta + \sqrt{2}\,(3\sin\vartheta - \sin 3\vartheta)\sin 3\varphi]$
$\mathbf{S}^0\,[\bar{6}m2]$, $\tilde{\mathbf{S}}^0\,[\bar{3}m]$, $3 \parallel X_3$, $m \perp X_1$	$S^0_{112} = 1$, $S^0_{222} = -1$	$r = (1/4)\,(3\sin\vartheta - \sin 3\vartheta)\sin 3\varphi$
$\mathbf{N}^0\,[\infty/mm]$, $\tilde{\mathbf{N}}^0\,[\infty 2]$, $\infty \parallel X_3$	$N^0_{1111} = N^0_{2222} = 3/8$, $N^0_{3333} = 1$, $N^0_{1122} = 1/8$, $N^0_{1133} = N^0_{2233} = -1/2$	$r = (1/64)\,(9 + 20\cos 2\vartheta + 35\cos 4\vartheta)$
$\mathbf{N}^0\,[m3m]$, $\tilde{\mathbf{N}}^0\,[432]$, $4 \parallel X_1, X_2, X_3$	$N^0_{1111} = N^0_{2222} = N^0_{3333} = 1$, $N^0_{2233} = N^0_{3311} = N^0_{1122} = -1/2$	$r = (1/64)\,[9 + 20\cos 2\vartheta + 35\cos 4\vartheta + 5\,(3 - 4\cos 2\vartheta + \cos 4\vartheta)\cos 4\varphi]$
$\mathbf{N}^0\,[m3m]$, $\tilde{\mathbf{N}}^0\,[432]$, $3 \parallel X_3$, $2 \parallel X_1$	$N^0_{1111} = N^0_{2222} = -1/4$, $N^0_{3333} = -2/3$, $N^0_{1122} = -1/12$, $N^0_{1133} = N^0_{2233} = 1/3$, $N^0_{1123} = 5\sqrt{2}/6$, $N^0_{2223} = -5\sqrt{2}/6$	$r = -(1/96)\,[9 + 20\cos 2\vartheta + 35\cos 4\vartheta - 20\sqrt{2}\,(2\sin 2\vartheta - \sin 4\vartheta)\sin 3\varphi]$
$\mathbf{N}^0\,[\bar{4}2m]$, $\bar{4} \parallel X_3$, $2 \parallel X_1$	$N^0_{1111} = N^0_{2233} = 7/9$, $N^0_{2222} = N^0_{1133} = -7/9$	$r = -(7/72)\,(3 + 4\cos 2\vartheta - 7\cos 4\vartheta)\cos 2\varphi$

For notation see Table 47.3

properties of the isotropic and gyrotropic media. However, the Fumi method of direct verification is entirely inapplicable while the method of averaging over the group is fairly complicated in this case, since it is connected with integrating over the group. But the isotropic and gyrotropic tensors and pseudotensors are easily derived with the aid of the theory of algebraic invariants.

Obviously any tensor of the form

$$\delta_{i_1 i_2}\delta_{i_3 i_4} \ldots \delta_{i_{r-1} i_r} \tag{48.1}$$

is isotropic as are all its isomers. Consequently any linear combination of such tensors is also isotropic. An inverse theorem is also valid: any isotropic tensor of rank r can be represented as a linear combination of all possible isomers of the tensor (Gurevich, 1948)*. This theorem fully solves the problem of the construction of the general form of isotropic tensors.

All second-rank isotropic tensors are of the form

$$T_{ij} = a\delta_{ij}. \tag{48.2}$$

Since Kronecker's tensor δ_{ij} is symmetric in indices, the external symmetry $\infty\infty m$ of a second-rank tensor already predetermines the internal symmetry $[V^2]$ of this tensor.**

An isotropic fourth-rank tensor is a linear combination of the three isomers of tensor $\delta_{ij}\delta_{kl}$:

$$T_{ijkl} = a\delta_{ij}\delta_{kl} + b\delta_{ik}\delta_{jl} + c\delta_{il}\delta_{ik}: \tag{48.3}$$

All the non-zero components of this tensor

$$\begin{aligned} &T_{1111} = T_{2222} = T_{3333} = a + b + c, \\ &T_{2233} = T_{3311} = T_{1122} = T_{3322} = T_{1133} = T_{2211} = a, \\ &T_{2323} = T_{3131} = T_{1212} = T_{3232} = T_{1313} = T_{2121} = b, \\ &T_{2332} = T_{3113} = T_{1221} = T_{3223} = T_{1331} = T_{2112} = c \end{aligned} \tag{48.4}$$

are interconnected by the relation

$$T_{1111} = T_{2233} + T_{2323} + T_{2332}. \tag{48.5}$$

---

* These isomers are, generally speaking, not independent: of the 105 isomers of an isotropic tensor of rank eight only 91 isomers are independent, of the 945 isomers of a tenth-rank tensor 603 are independent.

** This circumstance is used in thermodynamics. In Sec. 57 special proof is given of the symmetry of the tensor of dielectric permittivity $\varkappa$ in isothermic and adiabatic processes; in other processes it is, generally speaking, not symmetric. But if its internal symmetry $[V^2]$ follows directly from the external one (this occurs not only in isotropic bodies but also in the cubic and rhombic systems, as well as in the higher subsystems of the trigonal, tetragonal, hexagonal systems and in textures), then for the media of a corresponding symmetry and thermodynamic proof of the symmetry of the dielectric permittivity tensor is obviously unnecessary, the main thing being that this tensor is symmetric not only under isothermic and adiabatic processes, but under any processes in general.

The internal symmetry of this tensor is characterized by equalities

$$T_{ijkl} = T_{klij} = T_{jilk} = T_{lkji}. \tag{48.6}$$

In theoretical crystal physics there are used fourth-rank tensors with internal symmetry $[[V^2]^2]$, $[V^2]^2$, $[V^4]$ and $V\,[V^3]$. Let us derive the general form of the corresponding isotropic tensors.

A fourth-rank isotropic tensor invariant with respect to the permutation of the first two indices, of the last two indices and also of the first pair of indices with the second pair, must satisfy, besides the equalities (48.6), also the equality $T_{ijkl} = T_{jikl}$, and for this it is necessary that $b = c$. Therefore, the general form of an isotropic tensor of internal symmetry $[[V^2]^2]$ is:

$$T_{ijkl} = a\delta_{ij}\delta_{kl} + b\,(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \tag{48.7}$$

The internal symmetry $[V^2]^2$ is less than $[[V^2]^2]$, i.e. each tensor invariant with respect to the internal symmetry group $[[V^2]^2]$ is also invariant with respect to the $[V^2]^2$ group. However, Tables 47.1 show that the number of the independent components of isotropic tensors with internal symmetry $[[V^2]^2]$ and $[V^2]^2$ is the same (and equal to 2). It follows from these two facts that the general form of these tensors is also the same. Therefore the general form of the isotropic tensors with internal symmetry $[V^2]^2$ is also characterized by formula (48.7).

For the same reasons formula (48.7) can also be used for isotropic tensors with internal symmetry $[V^4]$ and $V\,[V^3]$:

$$T_{ijkl} = a\,(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \tag{48.8}$$

The general sixth-rank isotropic tensor is represented by a linear combination of 15 isomers. Here is, for example, the form of an isotropic tensor of internal symmetry $[[V^2]^3]$:

$$\begin{aligned} L_{ijklmn} = {} & a\delta_{ij}\delta_{kl}\delta_{mn} + b\,(\delta_{ij}\delta_{km}\delta_{ln} + \delta_{ij}\delta_{kn}\delta_{lm} + \\ & + \delta_{im}\delta_{kl}\delta_{jn} + \delta_{in}\delta_{kl}\delta_{jm} + \delta_{ik}\delta_{jl}\delta_{mn} + \\ & + \delta_{il}\delta_{jk}\delta_{mn}) + c\,(\delta_{ik}\delta_{jm}\delta_{ln} + \delta_{ik}\delta_{jn}\delta_{lm} + \\ & + \delta_{il}\delta_{jm}\delta_{kn} + \delta_{il}\delta_{jn}\delta_{km} + \delta_{im}\delta_{jk}\delta_{ln} + \\ & + \delta_{im}\delta_{jl}\delta_{kn} + \delta_{in}\delta_{jk}\delta_{lm} + \delta_{in}\delta_{jl}\delta_{km}); \end{aligned} \tag{48.9}$$

coefficients a, b, c are expressed in terms of its components:

$$\begin{aligned} & a = L_{112233}, \quad b = \frac{1}{2}\,(L_{112222} - L_{112233}), \\ & c = \frac{1}{8}\,(L_{111111} + 2L_{112233} - 3L_{112222}). \end{aligned} \tag{48.10}$$

The isotropic tensors of the following ranks—eighth, tenth and so on—can be constructed by the same method, but, in distinction from

the discussed cases, the number L_r of linearly independent isomers of tensor (48.1) for rank $r \geqslant 8$ is less than their total number $N_r = r!/2^n n!$ $(n = r/2)$. Therefore the coefficients of isomers are not defined uniquely and an additional problem arises: to expand an isotropic tensor into linearly independent combinations of isomers of tensor (48.1). A similar problem arises for isotropic pseudotensors, and the method of its solution is discussed below in the instance of the simplest pseudotensor.

In distinction from isotropic tensors, isotropic pseudotensors have an odd rank. Any isotropic pseudotensor of rank r can be represented as a linear combination of isomers of pseudotensor

$$\delta_{i_1 i_2 i_3} \delta_{i_4 i_5} \ldots \delta_{i_{r-1} i_r}, \tag{48.11}$$

where $\delta_{i_1 i_2 i_3}$ is a Levi-Civita pseudotensor. The number of these isomers $N_r = r!/3!2^n n!$ where $n = (r-3)/2$. In the following table there is written for each rank r the number N_r of isotropic tensors of the form (48.1) or isotropic pseudotensors of the form (48.11) as well as the number L_r of those linearly independent among them*:

$r=$	1	2	3	4	5	6	7	8	9	10
$N_r=$	0	1	1	3	10	15	105	105	1260	945
$L_r=$	0	1	1	3	6	15	36	91	232	603

This table shows that it is unreasonable to represent even a fifth-rank isotropic pseudotensor of a general form as

$$P_{ijklm} = A\delta_{ijk}\delta_{lm} + B\delta_{ijl}\delta_{km} + C\delta_{ijm}\delta_{kl} + D\delta_{ikl}\delta_{jm} + E\delta_{ikm}\delta_{jl} + \\ + F\delta_{ilm}\delta_{jk} + G\delta_{jkl}\delta_{im} + H\delta_{jkm}\delta_{il} + K\delta_{jlm}\delta_{ik} + L\delta_{klm}\delta_{ij}, \tag{48.12}$$

because the written out ten isomers are interconnected by linear dependences, and coefficients $A, \ldots, L$ cannot be defined uniquely. Let us expand this pseudotensor into its symmetric and antisymmetric components:

$$P_{ijklm} = P_{(ij)k(lm)} + P_{[ij]k(lm)} + P_{(ij)k[lm]} + P_{[ij]k[lm]}. \tag{48.13}$$

The first term we find directly from (48.12):

$$P_{(ij)k(lm)} = a(\delta_{ikl}\delta_{jm} + \delta_{ikm}\delta_{jl} + \delta_{jkl}\delta_{im} + \delta_{jkm}\delta_{il}). \tag{48.14}$$

For the expansion of the second term we use the duality relation $\varepsilon\{V^2\}V[V^2] \sim V^2[V^2]$. Insofar as the isotropic tensor with internal symmetry $V^2[V^2]$ is defined by (48.7), the dual pseudotensor of $P_{[ij]k(lm)}$ is

$$P_{[ij]k(lm)} = \delta_{ijn}[b\delta_{nk}\delta_{lm} + c(\delta_{nl}\delta_{km} + \delta_{nm}\delta_{kl})] = \\ = b\delta_{ijk}\delta_{lm} + c(\delta_{ijl}\delta_{km} + \delta_{ijm}\delta_{kl}). \tag{48.15}$$

* To compute L_r the methods of the theory of group representation are used.

In the same way we find the expansion of the third term

$$P_{(ij)\,k\,[lm]} = d\delta_{klm}\delta_{ij} + e\,(\delta_{ilm}\delta_{jk} + \delta_{jlm}\delta_{ik}). \qquad (48.16)$$

And finally, for the notation of the fourth addend we use the relation $\varepsilon\,\{V^2\}\,V\,\{V^2\} \sim \varepsilon V^3$. This means that pseudotensor $P_{[ij]k[lm]}$ can be expressed in terms of a third-rank pseudotensor. Since $P_{[ij]\,k[lm]}$ is isotropic, the third-rank pseudotensor is also isotropic, and consequently, has the form $f\delta_{pkq}$. Therefore

$$P_{[ij]\,k\,[lm]} = f\delta_{ijp}\delta_{pkq}\delta_{qlm} = f\delta_{ijp}\,(\delta_{pl}\delta_{km} - \delta_{pm}\delta_{kl}) =$$
$$= f\,(\delta_{ijl}\delta_{km} - \delta_{ijm}\delta_{kl}). \qquad (48.17)$$

Adding together equalities (48.14)-(48.17) we obtain for pseudotensor P_{ijklm} the expansion

$$P_{ijklm} = a\,(\delta_{ikl}\delta_{jm} + \delta_{ikm}\delta_{jl} + \delta_{jkl}\delta_{im} + \delta_{jkm}\delta_{il}) +$$
$$+ b\delta_{ijk}\delta_{lm} + (c+f)\,\delta_{ijl}\delta_{km} + (c-f)\,\delta_{ijm}\delta_{kl} +$$
$$+ d\delta_{klm}\delta_{ij} + e\,(\delta_{ilm}\delta_{jk} + \delta_{jlm}\delta_{ik}) \qquad (48.18)$$

determined, in distinction from (48.12) by six independent coefficients $a, \ldots, f$. The meaning of the above transformations is that the expansion of pseudotensor P_{ijklm} into its symmetric and antisymmetric components allowed to use the duality relations with respect to the latter which made it possible to write the pseudotensor without extra coefficients.

Since the rotation group $\infty\infty$ is a subgroup of the orthogonal $\infty\infty m$ group, all the tensors and pseudotensors invariant with respect to the orthogonal group, i.e. the isotropic ones, are also invariant with respect to the rotation group. But there are such tensors which are invariant with respect to the rotation group, but are not invariant with respect to the orthogonal group. We shall call them *gyrotropic* tensors. They are all of an odd rank. Any gyrotropic tensor of rank r can be represented as a linear combination of isomers of tensor

$$e_{i_1 i_2 i_3}\delta_{i_4 i_5} \ldots \delta_{i_{r-1} i_r}; \qquad (48.19)$$

a gyrotropic tensor **e**, antisymmetric with respect to all three indices is described in detail in Sec. 42.

Finally, gyrotropic pseudotensors are of an even rank; any such pseudotensor of rank r can be represented as a linear combination of isomers of pseudotensor

$$\psi\delta_{i_1 i_2} \ldots \delta_{i_{r-1} i_r}, \qquad (48.20)$$

where ψ is a unit pseudoscalar equal to 1 in the right-hand system of coordinates and to -1 in the left-hand one.

Formulas (48.11) and (48.19) are linear with respect to the pseudotensor δ_{ijk} and tensor e_{ijk} respectively. The explanation for this is

that according to the theorem on isotropic tensors the quadratic combinations composed of these quantities are expressed in terms of Kronecker's tensors. The following formulas are valid exactly for a Levi-Civita pseudotensor

$$\delta_{ijk}\delta_{lmn} = \begin{vmatrix} \delta_{il} & \delta_{im} & \delta_{in} \\ \delta_{jl} & \delta_{jm} & \delta_{jn} \\ \delta_{kl} & \delta_{km} & \delta_{kn} \end{vmatrix}, \tag{48.21}$$

$$\delta_{ijm}\delta_{klm} = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}, \tag{48.22}$$

$$\delta_{ikl}\delta_{jkl} = 2\delta_{ij}, \tag{48.23}$$

$$\delta_{ijk}\delta_{ijk} = 6. \tag{48.24}$$

The same formulas hold for similar quadratic combinations composed of the components of tensor e_{ijk}. Formulas (48.21)-(48.24) can also be used for mixed quadratic combinations: $\delta_{ijk}e_{lmn}$, $\delta_{ijm}e_{klm}$ and so on, but their right-hand sides should then be multiplied by the unit pseudoscalar ψ.

For more details on the problems mentioned in this chapter see Bhagavantam, Venkatarayudu (1959); Shouten (1965); Hamermesh (1966); Wooster (1973)

Sec. 49. Small Strains of a Continuous Medium

When a continuous medium—isotropic or anisotropic—is strained, its particles, generally speaking, are displaced from their initial positions: a particle which prior to strain was at a point $\boldsymbol{r}$ with coordinates x_i appears as a result of strain, at a point $\boldsymbol{r}'$ with coordinates x_i'. Vector

$$\boldsymbol{u} = \boldsymbol{r}' - \boldsymbol{r}, \quad u_i = x_i' - x_i \tag{49.1}$$

is the *displacement vector*. Obviously, the strained condition of bodies is fully defined by the vector field $\boldsymbol{u}(\boldsymbol{r})$ specified in the whole volume occupied by the body. For a more lucid description of strain it is more convenient, however, to use other vector and tensor fields derived from the displacement field. To obtain an idea of the strain of a continuous medium it is necessary to consider a particle together with its infinitesimal vicinity. The strain of a body near the given particle can be conveniently divided mentally into three motions: (1) translational motion of the particle together with its vicinity from point $\boldsymbol{r}$ to point $\boldsymbol{r}'$; (2) rotation of the neighbourhood as a solid body, about a certain axis that passes through the particle, i.e. through point $\boldsymbol{r}'$; (3) the strain proper, i.e. such a displacement of some particles of the vicinity with respect to other ones under which the distance between them changes.

The translational motion of a particle together with its neighbourhood is defined by vector $\boldsymbol{u}(\boldsymbol{r})$. The other two motions are defined by the derivatives of the displacement vector with respect to the coordinates. These nine derivatives form a non-symmetric, generally speaking, *distortion tensor* $\boldsymbol{\gamma} = \partial\boldsymbol{u}/\partial\boldsymbol{r}$ with components $\gamma_{ik} = \partial u_i/\partial x_k$. With the aid of a transposed tensor $\boldsymbol{\gamma}^* = \operatorname{Grad}\boldsymbol{u}$ the distortion tensor can be resolved into a symmetric part

$$\boldsymbol{\varepsilon} = \frac{1}{2}\left(\frac{\partial\boldsymbol{u}}{\partial\boldsymbol{r}} + \operatorname{Grad}\boldsymbol{u}\right) = \operatorname{Def}\boldsymbol{u}, \quad \varepsilon_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right), \tag{49.2}$$

which is called *the tensor of small strains*, and an antisymmetric part

$$\boldsymbol{\omega} = \frac{1}{2}\left(\frac{\partial\boldsymbol{u}}{\partial\boldsymbol{r}} - \operatorname{Grad}\boldsymbol{u}\right), \quad \omega_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_k} - \frac{\partial u_k}{\partial x_i}\right), \tag{49.3}$$

called *the tensor of small rotations*. When the strains of crystals do not disrupt them, all the components of the distortion tensor are

usually small: $|\gamma_{ik}| \ll 1$, and consequently all the components of tensors $\boldsymbol{\varepsilon}$ and $\boldsymbol{\omega}$ are also small. Only such strains will be discussed in this book.

In the vicinity of the material particle which was situated prior to deformation at point $\boldsymbol{r}$, the displacements are

$$\begin{aligned} \boldsymbol{u}(\boldsymbol{r}+\delta\boldsymbol{r}) &= \boldsymbol{u}(\boldsymbol{r}) + \frac{\partial \boldsymbol{u}(\boldsymbol{r})}{\partial \boldsymbol{r}} \cdot \delta\boldsymbol{r} = \boldsymbol{u}(\boldsymbol{r}) + \boldsymbol{\omega}\cdot\delta\boldsymbol{r} + \boldsymbol{\varepsilon}\cdot\delta\boldsymbol{r}, \\ u_i(\boldsymbol{r}+\delta\boldsymbol{r}) &= u_i(\boldsymbol{r}) + \frac{\partial u_i(\boldsymbol{r})}{\partial x_k}\delta x_k = u_i(\boldsymbol{r}) + \omega_{ik}\delta x_k + \varepsilon_{ik}\delta x_k. \end{aligned} \tag{49.4}$$

Here $\boldsymbol{\omega} = \boldsymbol{\omega}(\boldsymbol{r})$ and $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}(\boldsymbol{r})$. The displacements $\delta\boldsymbol{u}$ of the particles in the neighbourhood of the chosen particle which was situated prior to the strain at point $\boldsymbol{r}$ are

$$\begin{aligned} \partial\boldsymbol{u}(\boldsymbol{r}+\delta\boldsymbol{r}) &= \boldsymbol{u}(\boldsymbol{r}+\delta\boldsymbol{r}) - \boldsymbol{u}(\boldsymbol{r}) = \boldsymbol{\omega}\cdot\delta\boldsymbol{r} + \boldsymbol{\varepsilon}\cdot\delta\boldsymbol{r}, \\ \delta u_i(\boldsymbol{r}+\delta\boldsymbol{r}) &= u_i(\boldsymbol{r}+\delta\boldsymbol{r}) - u_i(\boldsymbol{r}) = \omega_{ik}\delta x_k + \varepsilon_{ik}\delta x_k. \end{aligned} \tag{49.5}$$

As was shown in Sec. 42, to the antisymmetric tensor $\boldsymbol{\omega}$ can correspond its axial dual vector $\overset{\circ}{\boldsymbol{\varphi}}$ called *the vector of small rotations*, with components

$$\varphi_i = -\frac{1}{2}\delta_{ijk}\omega_{jk}, \tag{49.6}$$

with $\boldsymbol{\omega}\cdot\delta\boldsymbol{r} = \overset{\circ}{\boldsymbol{\varphi}} \times \delta\boldsymbol{r}$. Therefore

$$\delta\boldsymbol{u}(\boldsymbol{r}+\delta\boldsymbol{r}) = \overset{\circ}{\boldsymbol{\varphi}} \times \delta\boldsymbol{r} + \boldsymbol{\varepsilon}\cdot\delta\boldsymbol{r}. \tag{49.7}$$

To find the geometric meaning of the tensor of small rotations let us assume that $\boldsymbol{\varepsilon}(\boldsymbol{r}) = 0$. If $\delta\boldsymbol{\rho}$ is the component of vector $\delta\boldsymbol{r}$ perpendicular to vector $\overset{\circ}{\boldsymbol{\varphi}}$, then

$$\delta\boldsymbol{u}(\boldsymbol{r}+\delta\boldsymbol{r}) = \overset{\circ}{\boldsymbol{\varphi}} \times \delta\boldsymbol{\rho}; \quad \delta u = \varphi\delta\rho.$$

But this means that the displacement of each point $\boldsymbol{r} + \delta\boldsymbol{r}$ of the neighbourhood is proportional to the distance $\delta\rho$ from point $\boldsymbol{r} + \delta\boldsymbol{r}$ to an axis parallel to vector $\overset{\circ}{\boldsymbol{\varphi}}$ and passing through point $\boldsymbol{r}$. Moreover, the direction of this displacement is perpendicular both to the axis and to vector $\delta\boldsymbol{\rho}$ which connects this axis with the given point of the vicinity. This clearly means a rotation of the whole neighbourhood about the rotation axis. It can also be readily seen that the angle (in radians) and the direction of this rotation coincide with the length and the direction of axial vector $\overset{\circ}{\boldsymbol{\varphi}}$ respectively.

Substituting the components of the tensor of small rotations (49.3) into (49.6), we obtain

$$\varphi_i = -\frac{1}{4}\delta_{ijk}\left(\frac{\partial u_j}{\partial x_k} - \frac{\partial u_k}{\partial x_j}\right) = \frac{1}{4}\delta_{ijk}\frac{\partial u_k}{\partial x_j} - \frac{1}{4}\delta_{ijk}\frac{\partial u_j}{\partial x_k}.$$

In the second term we give other notation to dummy indices and then use the identity $\delta_{ikj} = -\delta_{ijk}$:

$$-\frac{1}{4}\delta_{ijk}\frac{\partial u_j}{\partial x_k} = -\frac{1}{4}\delta_{ijk}\frac{\partial u_k}{\partial x_j} = \frac{1}{4}\delta_{ijk}\frac{\partial u_k}{\partial x_j}.$$

So

$$\varphi_i = \frac{1}{2}\delta_{ijk}\frac{\partial u_k}{\partial x_j}, \quad \overset{\circ}{\varphi} = \frac{1}{2}\operatorname{curl} \boldsymbol{u}. \tag{49.8}$$

For finding the geometric meaning of tensor $\boldsymbol{\varepsilon}$, we write $\boldsymbol{\omega}(\boldsymbol{r}) = 0$. Then $\delta\boldsymbol{u}(\boldsymbol{r} + \delta\boldsymbol{r}) = \boldsymbol{\varepsilon}\cdot\delta\boldsymbol{r}$. $\boldsymbol{\varepsilon}$ can be represented as any symmetric second-rank tensor, as $\boldsymbol{\varepsilon} = \varepsilon_{(1)}\boldsymbol{p}_1\boldsymbol{p}_1 + \varepsilon_{(2)}\boldsymbol{p}_2\boldsymbol{p}_2 + \varepsilon_{(3)}\boldsymbol{p}_3\boldsymbol{p}_3$, where $\boldsymbol{p}_i\cdot\boldsymbol{p}_j = \delta_{ij}$. Let us first consider the case when $\varepsilon_{(1)} = \varepsilon \neq 0$, $\varepsilon_{(2)} = \varepsilon_{(3)} = 0$. We denote $\boldsymbol{p}_1\cdot\delta\cdot\boldsymbol{r} = \delta x_1$. Obviously in this case

$$\delta\boldsymbol{u}(\boldsymbol{r} + \delta\boldsymbol{r}) = \boldsymbol{\varepsilon}\delta x_1\boldsymbol{p}_1.$$

This means that the displacements of all points of the vicinity are parallel to vector $\boldsymbol{p}_1$ and proportional to the distances between the corresponding points and the plane $\delta x_1 = 0$ perpendicular to this vector. Thus in this case there occurs an elongation in the direction parallel to $\boldsymbol{p}_1$, in the ratio of $(1 + \varepsilon) : 1$.

In a general case, when all the eigenvalues of tensor $\boldsymbol{\varepsilon}$ differ from zero, there occurs a superposition of such elongations in three mutually perpendicular directions as shown in Fig. 49.1.

Let us see now how the distances change in the direction of an arbitrary unit vector $\boldsymbol{n}$. For this purpose it is necessary to calculate the change under strain of the distance from point $\boldsymbol{r}$ to point $\boldsymbol{r} + \delta\boldsymbol{r}$ for $\delta\boldsymbol{r} = \boldsymbol{n}\delta s$. Prior to the strain this distance was δs. As a result of the strain point $(\boldsymbol{r} + \boldsymbol{n}\delta s)$ will be displaced with respect to point $\boldsymbol{r}$ by vector $\delta\boldsymbol{u} = \boldsymbol{\varepsilon}\cdot\boldsymbol{n}\delta s$. The component of this vector in the direction $\boldsymbol{n}$ is $\boldsymbol{n}\cdot\delta\boldsymbol{u} = \boldsymbol{n}\cdot\boldsymbol{\varepsilon}\cdot\boldsymbol{n}\delta s$. The relative change of distances in the direction $\boldsymbol{n}$ due to small strain $\boldsymbol{\varepsilon}$ is thus

$$\frac{n\cdot\delta u}{\delta s} = \boldsymbol{n}\cdot\boldsymbol{\varepsilon}\cdot\boldsymbol{n} = \varepsilon_{ik}n_in_k, \tag{49.9}$$

where $\boldsymbol{n}$ is the unit vector.

It is also interesting to compute the relative change of volumes under strain. If in the vicinity of point $\boldsymbol{r}$ there is chosen a small rectangular parallelepiped with edges parallel to the eigenvectors* of tensor $\boldsymbol{\varepsilon}$ and equal to l_1, l_2, l_3, then under strain it will change into a rectangular parallelepiped with edges $l_1' = (1 + \varepsilon_{(1)})\,l_1$, $l_2' = (1 + \varepsilon_{(2)})\,l_2$, $l_3' = (1 + \varepsilon_{(3)})\,l_3$, so that the relative change of the volume is

$$\frac{\Delta V}{V} = \frac{l_1'l_2'l_3' - l_1l_2l_3}{l_1l_2l_3} = (1 + \varepsilon_{(1)})(1 + \varepsilon_{(2)})(1 + \varepsilon_{(3)}) - 1.$$

* This is assumed only for simplifying the calculations. A quite arbitrary small parallelepiped would have furnished the same result.

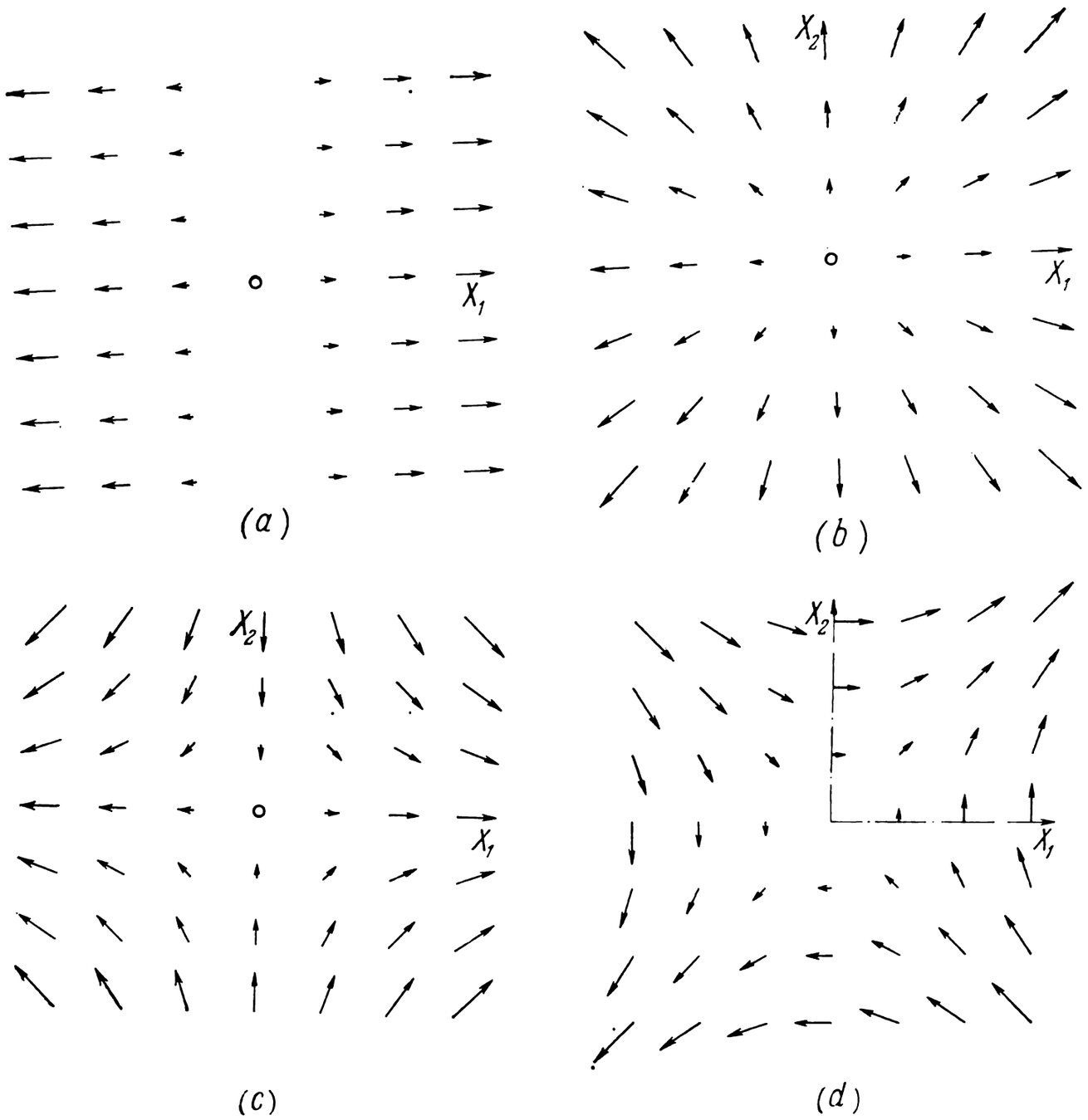


Fig. 49.1. Fields of the displacements vector $\boldsymbol{u}(\mathbf{r})$ at different homogeneous strains: (a) $\varepsilon = 0.2\boldsymbol{e}_1\boldsymbol{e}_1$, (b) $\varepsilon = 0.2\ (\boldsymbol{e}_1\boldsymbol{e}_1 + \boldsymbol{e}_2\boldsymbol{e}_2)$, (c) $\varepsilon = 0.2\ (\boldsymbol{e}_1\boldsymbol{e}_1 - \boldsymbol{e}_2\boldsymbol{e}_2)$; (d) $\varepsilon = 0.2\ (\boldsymbol{e}_1\boldsymbol{e}_2 + \boldsymbol{e}_2\boldsymbol{e}_1)$

If terms quadratic and cubic with respect to $\varepsilon_{(i)}$ are neglected, then

$$\frac{\Delta V}{V} = \varepsilon_{(1)} + \varepsilon_{(2)} + \varepsilon_{(3)} = \varepsilon_{kk}. \tag{49.10}$$

This expression, as was to be expected, does not depend on the choice of the coordinate system, being an invariant of the tensor of strains. It can also be easily expressed in terms of the displacement vector

$$\frac{\Delta V}{V} = \varepsilon_{kk} = \frac{\partial u_k}{\partial x_k} = \operatorname{div} \boldsymbol{u}. \tag{49.11}$$

It is instructive also to compute the alteration, resulting from strain, of the angle between two mutually orthogonal unit vectors $\boldsymbol{p}$ and $\boldsymbol{q}$ which prior to the strain were ($\boldsymbol{p}\cdot\boldsymbol{q} = 0$). After the strain the cosine of the angle between them is approximately

$$\cos\vartheta \approx (\boldsymbol{p} + \boldsymbol{\varepsilon}\cdot\boldsymbol{p})\cdot(\boldsymbol{q} + \boldsymbol{\varepsilon}\cdot\boldsymbol{q}) \approx 2\boldsymbol{p}\cdot\boldsymbol{\varepsilon}\cdot\boldsymbol{q}$$

(we have used not only the smallness but also the symmetry of tenser $\boldsymbol{\varepsilon}$). Thus

$$\vartheta \approx \frac{\pi}{2} - 2\boldsymbol{p}\cdot\boldsymbol{\varepsilon}\cdot\boldsymbol{q}. \tag{49.12}$$

The spherical part $1/3\varepsilon_{kk}\mathbf{I}$ of the strain tensor $\boldsymbol{\varepsilon}$ specifies the same change of volume as does the strain tensor itself, but the form does not change under the action of the spherical tensor: all the straight lines perpendicular before the strain remain so after it was applied: if $\boldsymbol{p}\cdot\boldsymbol{q} = 0$, then $\boldsymbol{p}\cdot 1/3\varepsilon_{kk}\mathbf{I}\cdot\boldsymbol{q} = 1/3\varepsilon_{kk}\boldsymbol{p}\cdot\boldsymbol{q} = 0$.

On the contrary, the deviator of the strain tensor

$$\mathbf{e} = \boldsymbol{\varepsilon} - \frac{1}{3}\varepsilon_{kk}\mathbf{I}, \quad e_{ij} = \varepsilon_{ij} - \frac{1}{3}\varepsilon_{kk}\delta_{ij}, \tag{49.13}$$

specifies strain which occurs without change of volume (since $e_{kk} = 0$); the change of the form, i.e. the skewness of right angles between initially perpendicular vectors is the same under strains $\boldsymbol{\varepsilon}$ and $\boldsymbol{e}$: if $\boldsymbol{p}\cdot\boldsymbol{q} = 0$, then $\boldsymbol{p}\cdot\boldsymbol{\varepsilon}\cdot\boldsymbol{q} = \boldsymbol{p}\cdot\mathbf{e}\cdot\boldsymbol{q}$.

If any field of displacements $\boldsymbol{u}(\boldsymbol{r})$ is given, the field of strains $\boldsymbol{\varepsilon} = \operatorname{Def}\boldsymbol{u}$ can be found. A question arises: can the vector field $\boldsymbol{u}(\boldsymbol{r})$ be restored from any tensor field $\boldsymbol{\varepsilon}(\boldsymbol{r})$, or, in other words, is any tensor field a strain of a certain vector field*. A similar situation we see in electrostatics: to any scalar function $\varphi(\boldsymbol{r})$ there corresponds a vector field $\boldsymbol{E} = -\operatorname{grad}\varphi$, but not any vector field at all is the gradient of a certain scalar field; it is known that for such a case the vector field must be irrotational: $\operatorname{curl}\boldsymbol{E} = 0$. It should be expected that a tensor field too must satisfy certain conditions in order to serve as a strain of some vector field. Let us derive these conditions.

Let us consider $\operatorname{Curl}\boldsymbol{\varepsilon}$. By definition

$$(\operatorname{Curl}\boldsymbol{\varepsilon})_{ij} = \delta_{ikl}\frac{\partial\varepsilon_{lj}}{\partial x_k}. \tag{49.14}$$

We express the components of this pseudotensor in terms of the displacement vector derivatives:

$$\delta_{ikl}\frac{\partial\varepsilon_{lj}}{\partial x_k} = \frac{1}{2}\delta_{ikl}\frac{\partial^2 u_l}{\partial x_k\,\partial x_j} + \frac{1}{2}\delta_{ikl}\frac{\partial^2 u_j}{\partial x_k\,\partial x_l}.$$

---

* It is assumed that u_i and ε_{jk} are sufficiently smooth functions of the coordinates.

The second term is identically zero, since functions $u_j(\boldsymbol{r})$ satisfy the requirements of the theorem on the change of the order of differentiation. Indeed, in this case tensor $\partial^2 u_j/\partial x_k\,\partial x_l$ is symmetric with respect to indices k and l, while tensor δ_{ikl} is antisymmetric with respect to these indices. Hence it is clear that $\delta_{ikl}\,\partial^2 u_j/\partial x_k\,\partial x_l = 0$. But $\delta_{ikl}\,\partial^2 u_j/\partial x_k\,\partial x_l = (\text{Curl Grad}\,\boldsymbol{u})_{ij}$, so that we obtain a formula of tensor analysis

$$\text{Curl Grad} = 0. \tag{49.15}$$

Having noticed that $\delta_{ikl}\,\partial u_l/\partial x_k = (\text{curl}\,\boldsymbol{u})_i$ we write (49.14) as

$$(\text{Curl}\,\boldsymbol{\varepsilon})_{ij} = \frac{1}{2}\frac{\partial(\text{Curl}\,\boldsymbol{u})_i}{\partial x_j}, \quad \text{Curl}\,\boldsymbol{\varepsilon} = \frac{1}{2}\frac{\partial(\text{Curl}\,\boldsymbol{u})}{\partial \boldsymbol{r}}. \tag{49.16}$$

On the other hand, $1/2\,\text{curl}\,\boldsymbol{u} = \overset{\circ}{\boldsymbol{\varphi}}$. So we obtain an important formula

$$(\text{Curl}\,\boldsymbol{\varepsilon})_{ij} = \frac{\partial\varphi_i}{\partial x_j}, \quad \text{Curl}\,\boldsymbol{\varepsilon} = \frac{\partial\overset{\circ}{\boldsymbol{\varphi}}}{\partial \boldsymbol{r}}. \tag{49.17}$$

Its importance is not restricted to this instance alone, we shall use it in the future. The relations sought for are now easily derived. We transpose both parts of (49.17), obtain $(\text{Curl}\,\boldsymbol{\varepsilon})^* = \text{Grad}\,\overset{\circ}{\boldsymbol{\varphi}}$ and subject both parts of the obtained equality to operation Curl. Since $\text{Curl}\,(\text{Curl}\,\boldsymbol{\varepsilon})^* = \text{Inc}\,\boldsymbol{\varepsilon}^*$ and, as has already been noted, $\text{Curl Grad} = 0$, we finally obtain

$$\text{Inc}\,\boldsymbol{\varepsilon} = 0, \quad \delta_{ikm}\delta_{iln}\frac{\partial^2\varepsilon_{mn}}{\partial x_k\,\partial x_l} = 0. \tag{49.18}$$

So, it has been proved that if a tensor field is a strain of a certain vector field, then its incompatibility vanishes. Equations (49.18) are called the *Saint-Venant's compatibility equations.*

We have only proved the necessity of these equations. If $\text{Inc}\,\varepsilon = 0$, then the displacement field can be defined from the tensor field $\varepsilon(\boldsymbol{r})$, which proves the sufficiency of the equations. For an unambiguous determination of displacements it is also necessary to fix the position of the body, i.e. to eliminate the possibility of its movement as a whole. Let us fix for this purpose an arbitrary point $\boldsymbol{r}^{(0)}$ of the body, i.e. specify at this point displacement $\boldsymbol{u}(\boldsymbol{r}^{(0)}) = 0$ and rotations $\boldsymbol{\varphi}(\boldsymbol{r}^{(0)})$. By a transformation of coordinates it is possible to make $\boldsymbol{r}^{(0)} = 0$, $\boldsymbol{u}(\boldsymbol{r}^{(0)}) = 0$, and $\boldsymbol{\varphi}(\boldsymbol{r}^{(0)}) = 0$. Then the displacements at any point r are computed with the aid of the Kirchhoff-Volterra-Cesaro formula which in this case (we give it without derivation) takes the form:

$$\boldsymbol{u}(\boldsymbol{r}) = \int_0^{\boldsymbol{r}} (\varepsilon - \boldsymbol{r}' \times \text{Curl}\,\varepsilon)\,d\boldsymbol{r}',$$

$$u_i(\boldsymbol{r}) = \int_0^{\boldsymbol{r}} \left(\varepsilon_{ij} - \delta_{ikl}r'_k\delta_{lmn}\frac{\partial\varepsilon_{nj}}{\partial x_m}\right) dx'_j.$$

* A second-order differential operation expressed by relation (49.18) is called *incompatibility* and denoted Inc.

The line integral in these formulas is taken along any line passing within the strained body and connecting the point $\boldsymbol{r}^{(0)} = 0$ with point $\boldsymbol{r}$. The argument of the integrand is a variable vector $\boldsymbol{r}'$, with coordinates x_i' which passes through all possible values along this line. The Saint-Venant's compatibility equations are actually the conditions ensuring the integration of equations $\varepsilon = \operatorname{Def} \boldsymbol{u}$, i.e. they ensure the independence of the line integral in the Kirchhoff-Volterra-Cesaro formula from the path of integration.

Let us consider the compatibility equations of strains for the case when the strain tensor depends on a single coordinate only, say, on x_3. Then

$$\frac{d^2\varepsilon_{11}}{dx_3^2} = \frac{d^2\varepsilon_{22}}{dx_3^2} = \frac{d^2\varepsilon_{12}}{dx_3^2} = 0, \tag{49.19}$$

and the other three compatibility equations are satisfied identically. From (49.19) it follows that ε_{11}, ε_{22} and ε_{12} are linearly dependent on x_3:

$$\varepsilon_{\alpha\beta} = A_{\alpha\beta} + B_{\alpha\beta}x_3 \quad (\alpha, \beta = 1, 2;\ A_{\alpha\beta} = A_{\beta\alpha},\ B_{\alpha\beta} = B_{\beta\alpha}). \tag{49.20}$$

When the strain tensor depends on a single coordinate, all the compatibility equations come to relations (49.20).

Sec. 50. Stress Tensor

When a crystal is strained, there develop forces tending to restore its initial configuration. These forces, as is shown by the crystal lattice theory, are short-ranged ones: their effective radius does not exceed several parameters of the lattice (piezoelectric crystals are not considered here: their properties will be discussed later). But the elementary volumes used in the theory of continuous media are large in comparison with unit cells of a crystal; therefore it should be assumed that a force acting as a result of strain on any volume isolated mentally in a crystal is transmitted only across the surface that bounds this volume. Then the stress at each point of the crystal* is characterized by aggregate of forces $\boldsymbol{P}\,dS$ acting upon all the possible figures passing through this point, with a unit vector of the external normal $\boldsymbol{n}$ and area dS (vector $\boldsymbol{P}$ has the same dimensionality as stress force divided by area).

Thus the stress at a point is defined by the function $\boldsymbol{P}(\boldsymbol{n})$, or, if notation $\boldsymbol{F} = \boldsymbol{P}\,dS$, $\boldsymbol{N} = \boldsymbol{n}\,dS$ is introduced by the function $\boldsymbol{F}(\boldsymbol{N})$. Let us prove that this function is linear. The equality $\boldsymbol{F}(\lambda\boldsymbol{N}) = \lambda\boldsymbol{F}(\boldsymbol{N})$, where λ is an arbitrary (but not too large) real number, follows directly from the definition of vectors $\boldsymbol{F}$ and $\boldsymbol{N}$. Now let us imagine that a plane figure, characterized by vector $\boldsymbol{N}$,

* As always in mechanics of continuous media, the term 'point' means elementary volume.

is approximated by a ribbed surface whose individual areas are characterized by vectors $\boldsymbol{N}_s$. Geometric considerations show that in this case $\sum \boldsymbol{N}_s = \boldsymbol{N}_s$. From physical considerations it follows that the total force acting on the figure should not essentially depend on its being plane or ribbed, i.e. $\sum \boldsymbol{F}(\boldsymbol{N}_s) = \boldsymbol{F}(\boldsymbol{N})$. Having combined these two equalities we obtain $\boldsymbol{F}(\sum \boldsymbol{N}_s) = \sum \boldsymbol{F}(\boldsymbol{N}_s)$, this completing the proof.

Since vector $\boldsymbol{F}$ is a linear function of vector $\boldsymbol{N}$, there is a second-rank tensor $\boldsymbol{\sigma}$ which does not depend on $\boldsymbol{N}$, such that $\boldsymbol{F} = \boldsymbol{\sigma}\cdot\boldsymbol{N}$ (see Sec. 18) or, returning to the initial notation

$$\boldsymbol{P} = \boldsymbol{\sigma}\cdot\boldsymbol{n}, \quad P_i = \sigma_{ij}n_j. \tag{50.1}$$

Tensor $\boldsymbol{\sigma}$ is called the *stress tensor*; fully specifying function $\boldsymbol{P}(\boldsymbol{n})$, it exhaustively describes the stress at a point. To find it, it will suffice to measure forces $\boldsymbol{P}^{(k)}$ acting on three figures with non-coplanar normals $\boldsymbol{n}^{(k)}$; then the components σ_{ij} are the solution of a set of nine linear equations

$$n_j^{(k)}\sigma_{ij} = P_i^{(k)}. \tag{50.2}$$

Let, in particular, the normals to figures be parallel to mutually orthogonal unit vectors: $\boldsymbol{n}^{(k)} = \boldsymbol{e}_k$. Then $n_j^{(k)} = \delta_{jk}$, so that system (50.2) becomes

$$\sigma_{ik} = P_i^{(k)}. \tag{50.3}$$

Thus, σ_{ik} is the i-th component of the force applied to a unit area, the external normal to which is directed along axis X_k.

Since the force acting on a 1 sq·cm of a figure with an external normal $\boldsymbol{n}$ is $\boldsymbol{P} = \boldsymbol{\sigma}\cdot\boldsymbol{n}$, the normal component of this force $\boldsymbol{n}\cdot\boldsymbol{P} = \boldsymbol{n}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n} = \sigma_{ik}n_in_k$, while the total shear component (i.e. one lying in the plane of the figure) $\boldsymbol{P} - \boldsymbol{nn}\cdot\boldsymbol{P} = (\mathbf{I} - \boldsymbol{nn})\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n}$. The shear stress in the specified direction $\boldsymbol{l}$ is $\boldsymbol{l}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n} = \sigma_{ik}l_in_k$; the unit vector $\boldsymbol{l}$ lies in the plane of the figure and is therefore perpendicular to vector $\boldsymbol{n}$.

Let us mentally isolate some volume V of a body bounded by surface S. If force $\boldsymbol{P}\,dS = \boldsymbol{\sigma}\cdot\boldsymbol{n}\,dS$ acts upon each element dS of the surface, then upon the whole volume there acts a force

$$\boldsymbol{F} = \oint_S \boldsymbol{P}\,dS = \oint_S \boldsymbol{\sigma}\cdot\boldsymbol{n}\,dS, \quad F_i = \oint_S P_i\,dS = \oint_S \sigma_{ik}n_k\,dS. \tag{50.4}$$

The integral over a closed surface, according to the Gauss-Ostrogradsky theorem (see Sec. 43) can be transformed into an integral taken over space bounded by this surface:

$$\boldsymbol{F} = \oint_S \boldsymbol{\sigma}\cdot\boldsymbol{n}\,dS = \int_V \operatorname{Div}\boldsymbol{\sigma}^*\,dV, \quad F_i = \oint_S \sigma_{ik}n_k\,dS = \int_V \frac{\partial\sigma_{ik}}{\partial x_k}\,dV. \tag{50.5}$$

On the other hand, according to Newton's second law

$$\boldsymbol{F} = \int_V \rho \frac{\partial^2 \boldsymbol{u}}{\partial t^2} dV, \quad F_i = \int_V \rho \frac{\partial^2 u_i}{\partial t^2} dV. \tag{50.6}$$

Comparing this with (50.5), we obtain

$$\int_V \operatorname{Div} \boldsymbol{\sigma}^* dV = \int_V \rho \frac{\partial^2 \boldsymbol{u}}{\partial t^2} dV, \quad \int_V \frac{\partial \sigma_{ik}}{\partial x_k} dV = \int_V \rho \frac{\partial^2 u_i}{\partial t^2} dV.$$

Since this equality holds for any choice of volume V, the integrands must be equal to each other respectively:

$$\operatorname{Div} \boldsymbol{\sigma}^* = \rho \frac{\partial^2 \boldsymbol{u}}{\partial t^2}, \quad \frac{\partial \sigma_{ik}}{\partial x_k} = \rho \frac{\partial^2 u_i}{\partial t^2}. \tag{50.7}$$

These equations of motion of an elastic body are the so-called equations of *elastodynamics* or the *Cauchy* relations. The equations of the equilibrium of an elastic body, the equations of *elastostatics*,

$$\operatorname{Div} \boldsymbol{\sigma}^* = 0, \quad \frac{\partial \sigma_{ik}}{\partial x_k} = 0, \tag{50.8}$$

are their important special case. If a body is acted upon also by a body force $\boldsymbol{f}$ (the dimension of this vector is force/volume), it must be added to the left-hand sides of equations (50.7) and (50.8). For instance, when body forces are present, the Cauchy equations take the form:

$$\operatorname{Div} \boldsymbol{\sigma}^* + f = \rho \frac{\partial^2 \boldsymbol{u}}{\partial t^2}, \quad \frac{\partial \sigma_{ik}}{\partial x_k} + f_i = \rho \frac{\partial^2 u_i}{\partial t^2}. \tag{50.9}$$

Let us now compute the moment of force acting upon the mentally isolated volume V with surface S. With account taken of the solid forces it equals

$$\begin{aligned} \boldsymbol{M} &= \oint_S \boldsymbol{r} \times \boldsymbol{P}\, dS + \int_V \boldsymbol{r} \times \boldsymbol{f}\, dV, \\ M_i &= \oint_S \delta_{ijk} x_j P_k\, dS + \int_V \delta_{ijk} x_j f_k\, dV. \end{aligned} \tag{50.10}$$

Further calculations are more conveniently done in a coordinate form. We express the surface forces P_k in terms of the stress tensor and transform the surface integral into a volume one

$$\oint_S x_j P_k\, dS = \oint_S x_j \delta_{kl} n_l\, dS = \int_V \frac{\partial (x_j \sigma_{kl})}{\partial x_l} dV.$$

Noting that $\partial (x_j\sigma_{kl})/\partial x_l = x_j\, \partial\sigma_{kl}/\partial x_l + \sigma_{kl}\, \partial x_j/\partial x_l$, with $\partial x_j/\partial x_l = \delta_{jl}$, so that $\sigma_{kl}\, \partial x_j/\partial x_l = \sigma_{kj}$, we rewrite (50.10) as follows:

$$M_i = \int\limits_V \delta_{ijk} x_j \left(\frac{\partial\sigma_{kl}}{\partial x_l} + f_k \right) dV + \int\limits_V \delta_{ijk}\sigma_{kj}\, dV. \qquad (50.11)$$

In the integrand of the first integral the sum in brackets is equal to the force acting on unit volume of the body (cf. equation (50.9)), while the whole integrand is equal to its moment. Thus, the entire action of the moments of surface and solid forces upon the chosen volume is reduced to the first integral, while the second integral should be zero. From the arbitrary character of volume V it follows that the integrand vanishes:

$$\delta_{ijk}\sigma_{kj} = 0. \qquad (50.12)$$

These three equalities mean that the stress tensor $\boldsymbol{\sigma}$ is symmetric. Actually, expanding the first of them we obtain $\delta_{ijk}\sigma_{kj} = \sigma_{32} - \sigma_{23} = 0$, while the second and third yield $\sigma_{13} - \sigma_{31} = 0$, $\sigma_{21} - \sigma_{12} = 0$.

Lately there have been studied models of continuous media with internal degrees of freedom in which the stress tensor may not be symmetric. Let us imagine, for instance, a continuous medium with uniformly disseminated particles capable of rotating with respect to the medium, this process gives rise to forces which tend to restore the particles to their initial positions. Such, for example, is the case of magnetized or electrically polarized particles disseminated in a continuous medium. If this medium is placed in an electric or a magnetic field, a torque will be exerted on each particle; the sum of all the moments acting on the particles contained in unit volume is called the *body moment* $\boldsymbol{m}$. Moreover, the moment can be transmitted across the surface: on unit area with an external normal $\boldsymbol{n}$ there acts a surface moment $\boldsymbol{Q}$ related to the pseudotensor of moment stresses $\boldsymbol{\mu}$ in the same way as the surface forces $\boldsymbol{P}$ with the stress tensor $\boldsymbol{\sigma}$:

$$\boldsymbol{Q} = \boldsymbol{\mu}\cdot\boldsymbol{n}.$$

For such media equality (50.10) is replaced by the following one:

$$M_i = \oint\limits_S \delta_{ijk} x_j P_k\, dS + \int\limits_V \delta_{ijk} x_j f_k + \oint\limits_S Q_i\, dS \quad \int\limits_V m_i\, dV.$$

Then instead of (50.11), we obtain

$$M_i = \int\limits_V \delta_{ijk} x_j \left(\frac{\partial\sigma_{kl}}{\partial x_l} + f_k \right) dV + \int\limits_V \left(\frac{\partial\mu_{il}}{\partial x_l} + m_i - \delta_{ijk}\sigma_{jk} \right) dV.$$

Obviously the integrand in the second integral has the meaning of the total moment acting on the particles in a unit volume. Due to the smallness of inertia moments of the particles it can be assumed to be zero, so that the antisymmetric part of the stress tensor is

$$\delta_{ijk}\delta_{jk} = \frac{\partial\mu_{il}}{\partial x_l} + m_i.$$

Thus the antisymmetric part of the stress tensor balances the body moments and the moment generated by moment stresses. In the absence of body-moments and moment stresses the stress tensor $\boldsymbol{\sigma}$ is symmetric *. For this refer to Aero and Kuvshinsky (1960), Kuvshinsky and Aero (1963), Palmov (1964).

Let us derive the mean values of the stress tensor

$$\langle \boldsymbol{\sigma} \rangle = \frac{1}{V} \int_V \boldsymbol{\sigma}\, dV, \quad \langle \sigma_{ik} \rangle = \frac{1}{V} \int_V \sigma_{ik}\, dV \tag{50.13}$$

and of its moment

$$\langle \boldsymbol{r} \times \boldsymbol{\sigma} \rangle = \frac{1}{V} \int_V \boldsymbol{r} \times \boldsymbol{\sigma}\, dV, \quad \langle \delta_{ijk} x_j \sigma_{kl} \rangle = \frac{1}{V} \int_V \delta_{ijk} x_j \sigma_{kl}\, dV \tag{50.14}$$

for an elastic body which is in equilibrium under loads $\boldsymbol{P}$ applied to its surface.

Let us consider the divergence $\frac{\partial}{\partial x_l}(x_k \sigma_{il}) = \frac{\partial x_k}{\partial x_l} \sigma_{il} + x_k \frac{\partial \sigma_{il}}{\partial x_l}$. Since $\partial x_k / \partial x_l = \delta_{kl}$, the first term is σ_{ik}. The second term is zero due to the equations of equilibrium. Therefore the mean value of the stress tensor is expressed in terms of a surface integral

$$\langle \sigma_{ik} \rangle = \frac{1}{V} \int_V \sigma_{ik}\, dV = \frac{1}{V} \int_V \frac{\partial}{\partial x_l}(x_k \sigma_{il})\, dV =$$

$$= \frac{1}{V} \oint_S x_k \sigma_{il} n_l\, dS = \frac{1}{V} \int_S P_i x_k\, dS.$$

So

$$\langle \sigma_{ik} \rangle = \frac{1}{V} \oint_S P_i x_k\, dS, \quad \langle \boldsymbol{\sigma} \rangle = \frac{1}{V} \oint_S \boldsymbol{P}\boldsymbol{r}\, dS. \tag{50.15}$$

Now let us consider the divergence

$$\frac{\partial}{\partial x_m}(x_j x_l \sigma_{km}) = \frac{\partial x_j}{\partial x_m} x_l \sigma_{km} + x_j \frac{\partial x_l}{\partial x_m} \sigma_{km} + x_j x_l \frac{\partial \sigma_{km}}{\partial x_m}.$$

Reasoning as in the preceding deduction, we find that

$$\frac{\partial}{\partial x_m}(x_j x_l \sigma_{km}) = x_l \sigma_{kj} + x_j \sigma_{kl}.$$

Let us notice now that

$$\delta_{ijk} \frac{\partial}{\partial x_m}(x_j x_l \sigma_{km}) = \delta_{ijk} x_j \sigma_{kl},$$

* It can be easily verified that taking account of the moments of the body forces will not change this conclusion. If there exist body-moments, however, their density will obviously be $m_i = -\delta_{ijk}\sigma_{kj} = \delta_{ijk}\sigma_{jk}$, and in this case the stress tensor will never be symmetric. We shall not discuss such cases.

because $\delta_{ijk}\sigma_{kj} = 0$ due to the symmetry of the stress tensor. This allows expressing in terms of the surface integral the mean value of the stress tensor moment as well:

$$\langle \delta_{ijk} x_j \sigma_{kl} \rangle = \frac{1}{V} \oint_S \delta_{ijk} x_j P_k x_l \, dS,$$
$$\langle \boldsymbol{r} \times \boldsymbol{\sigma} \rangle = \frac{1}{V} \oint_S \boldsymbol{r} \times \boldsymbol{P}\boldsymbol{r} \, dS. \tag{50.16}$$

Thus the mean values of the stress tensor and its moment can be found with the aid of surface loads, without solving the equations of the theory of elasticity. The obtained result is especially important in those cases when the surface of the body is free of loads. In this case the stress tensor field is self-balanced: the tensor itself may differ from zero, but its mean values and those of its moment must be zero. Hence it follows, in particular, that if any tensor component (or its moment) is not identically zero, it always changes its sign, i.e. it must assume both positive and negative values.

Sec. 51. Generalized Hooke's Law

Let us compute the work of external forces $\boldsymbol{P}$ applied to the surface S of an elastic body of volume V. If under the action of these forces the surface points experience small displacements $\delta\boldsymbol{u}$, then the work

$$\delta A = \oint_S \delta\boldsymbol{u} \cdot \boldsymbol{P} \, dS = \oint_S \delta u_i P_i \, dS.$$

Since $\boldsymbol{P} = \boldsymbol{\sigma} \cdot \boldsymbol{n}$, where $\boldsymbol{n}$ is the unit vector of the external normal to the surface S, then

$$\delta A = \oint_S \delta\boldsymbol{u} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{n} \, dS = \oint_S \delta u_i \sigma_{ij} n_j \, dS.$$

Let us transform, as we did in Sec. 50, the surface integral into a volume one:

$$\delta A = \int_V \operatorname{div} (\delta\boldsymbol{u} \cdot \boldsymbol{\sigma}) \, dV = \int_V \frac{\partial}{\partial x_j} (\delta u_i \sigma_{ij}) \, dV.$$

According to the rule of differentiating a product

$$\delta A = \int_V \frac{\partial \delta u_i}{\partial x_j} \sigma_{ij} \, dV + \int_V \delta u_i \frac{\partial \sigma_{ij}}{\partial x_j} \, dV. \tag{51.1}$$

The space derivatives of small displacements $\partial (\delta u_i)/\partial x_j$ are equal to small distortions $\delta\varepsilon_{ij} + \delta\omega_{ij}$, but since the contraction of an anti-

symmetric tensor $\delta\omega_{ij}$ with a symmetric tensor σ_{ij} is an identical zero, the first integrand from (51.1) reduces to $\sigma_{ij}\sigma\varepsilon_{ij}$.

Let us pass to the second integral. According to equations of elastodynamics, $\partial\sigma_{ij}/\partial x_j = \rho\ddot{u}_i$, while δu_i can be regarded as $\dot{u}_i\delta t$ where δt is the time during which the displacements $\delta \boldsymbol{u}$ occur. Next, $\rho\ddot{u}_i\dot{u}_i\delta t = (1/2)\,\rho\cdot\partial/\partial t\,(\dot{u}_i\dot{u}_i)\ \delta t$, but this is the variation of kinetic energy of unit volume during the time δt (according to the approximation assumed in the theory of small strains density ρ remains constant in the process of straining). Then the second integral from (51.1) is the variation of the total kinetic energy K of an elastic body. Thus, the work of external forces

$$\delta A = \int\limits_V \sigma_{ij}\delta\varepsilon_{ij}dV + \delta K,$$

so that a part of work spent on applying a small strain $\delta\varepsilon_{ij}$ to unit volume of the body (or, for greater generality, on changing the strain of unit volume by a small magnitude $\delta\varepsilon_{ij}$), becomes equal to

$$\delta R = \sigma_{ij}\delta\varepsilon_{ij}. \tag{51.2}$$

In elastic (more exactly, linearly elastic) bodies each stress component is proportional to each strain component. With respect to crystals this means that the stress tensor is linearly related to the strain tensor, and this linear dependence

$$\sigma_{ij} = c_{ijkl}\varepsilon_{kl}, \quad \boldsymbol{\sigma} = \mathbf{c} : \boldsymbol{\varepsilon} \tag{51.3}$$

is specified by a matter tensor $\mathbf{c}$; it is called *the tensor of the elasticity coefficients* or *of the stiffness coefficients* and is expressed in kgf/cm^2, dyn/cm^2 or N/m^2.

To find the work necessary for a finite variation of the strain of unit volume of an elastic anisotropic body from $\boldsymbol{\varepsilon}^{(0)}$ to $\boldsymbol{\varepsilon}^{(1)}$ it is necessary to integrate (51.2) taking account of (51.3):

$$R = \int\limits_{\varepsilon^{(0)}}^{\varepsilon^{(1)}} c_{ijkl}\varepsilon_{kl}\,d\varepsilon_{ij}.$$

This integral, generally speaking, depends on the path of integration; the condition of its independence from the latter is the existence of such a function $W(\boldsymbol{\varepsilon})$ that

$$\mathbf{c} : \boldsymbol{\varepsilon} = \frac{\partial W}{\partial \varepsilon}, \qquad c_{ijkl}\varepsilon_{kl} = \frac{\partial W}{\partial \varepsilon_{ij}}. \tag{51.4}$$

Then the work on elastic straining of the unit volume will equal

$$R = \int\limits_{\varepsilon^{(0)}}^{\varepsilon^{(1)}} c_{ijkl}\varepsilon_{kl}\,d\varepsilon_{ij} = W(\varepsilon^{(1)}) - W(\varepsilon^{(0)}),$$

so that function $W(\varepsilon)$ will be the density of the elastic strain energy. If we assume that $W(0) = 0$ it equals

$$W = \frac{1}{2} c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} = \frac{1}{2} \varepsilon : \mathbf{c} : \varepsilon. \tag{51.5}$$

It also follows from (51.4) that

$$c_{ijkl} = \frac{\partial^2 W}{\partial\varepsilon_{ij}\,\partial\varepsilon_{kl}}, \qquad \mathbf{c} = \frac{\partial^2 W}{\partial\varepsilon\,\partial\varepsilon}, \tag{51.6}$$

this meaning that $c_{ijkl} = c_{klij}$. Taking into account the internal symmetry $[V^2]$ of the tensor ε ($\varepsilon_{ij} = \varepsilon_{ji}$) (see Sec. 42), we see that if the relation (51.4) is satisfied, the internal symmetry of tensor $\mathbf{c}$ is $[[V^2]^2]$:

$$c_{ijkl} = c_{jikl} = c_{ijlk} = c_{klij}. \tag{51.7}$$

Relation (51.4), as it follows from Chapter VII, is in particular satisfied in such important cases as the adiabatic and isothermal strain of crystals.

In formulas (51.3), (51.5) and (51.6) it is convenient to replace the pairs of indices ij and kl by Greek indices λ and μ taking the values of 1, . . ., 6. The method of changing to such a notation is described in Appendix F. Thereupon the formulas will appear respectively as:

$$\sigma_\lambda = c_{\lambda\mu}\varepsilon_\mu, \tag{51.3'}$$

$$W = \frac{1}{2} c_{\lambda\mu}\varepsilon_\lambda\varepsilon_\mu, \tag{51.5'}$$

$$c_{\lambda\mu} = \frac{\partial^2 W}{\partial\varepsilon_\lambda\,\partial\varepsilon_\mu} \tag{51.6'}$$

Relation (51.3) can be rewritten, expressing strains as the functions of stresses:

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}, \quad \varepsilon = \mathbf{s} : \sigma, \quad \varepsilon_\lambda = s_{\lambda\mu}\sigma_\mu; \tag{51.8}$$

$\mathbf{s}$ is the *tensor of compliance coefficients* (or elastic moduli); its internal symmetry is of course the same as that of tensor $\mathbf{c}$, the tensor $\mathbf{c}$ is expressed in cm^2/dyn, cm^2/kgf or m^2/N.

Relations (51.3) and (51.8) are called the *generalized Hooke's law for anisotropic media.* If thermal expansion of the crystal is to be also taken into account, the relations are supplemented by temperature terms.

Under uniform temperature variation by Θ degrees a crystal, free of external loads, experiences a temperature strain

$$\varepsilon_{ij} = \alpha_{ij}\Theta, \quad \varepsilon_\lambda = \alpha_\lambda\Theta;$$

α is the tensor of the thermal expansion coefficients, obviously it is symmetric as well as tensor ε; its dimensionality is K^{-1}.

In a general case, when a crystal experiences both mechanical stresses and temperature variations, the tensor of small strains is composed of parts caused by each of the above agents separately:

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl} + \alpha_{ij}\Theta, \quad \varepsilon_\lambda = s_{\lambda\mu}\sigma_\mu + \alpha_\lambda\Theta. \tag{51.9}$$

Then the temperature terms appear also in the expression for stresses:

$$\sigma_{ij} = c_{ijkl}\varepsilon_{kl} - \beta_{ij}\Theta, \quad \sigma_\lambda = c_{\lambda\mu}\varepsilon_\mu - \beta_\lambda\Theta; \tag{51.10}$$

$\boldsymbol{\beta}$ is called the *tensor of thermoelasticity coefficients*; it is symmetric, as well as $\boldsymbol{\alpha}$.

Let us derive the relations between the matter tensors included in the generalized Hooke's law with temperature terms (51.9), (51.10). Substituting into (51.10) the strains expressed by (51.9), we obtain

$$\sigma_\lambda = c_{\lambda\mu}s_{\mu\nu}\sigma_\nu - (\beta_\lambda - c_{\lambda\mu}\alpha_\mu)\,\Theta.$$

Since this identity should hold at arbitrary values of stresses σ_λ and temperature Θ, hence follow the relations sought:

$$c_{\lambda\mu}s_{\mu\nu} = \delta_{\lambda\nu}, \quad c_{ijkl}s_{klmn} = \frac{1}{2}(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm}), \tag{51.11}$$

$$\beta_\lambda = c_{\lambda\mu}\alpha_\mu, \quad \beta_{ij} = c_{ijkl}\alpha_{kl}. \tag{51.12}$$

In the formulations of Hooke's law (51.3) and (51.10) (but not (51.8) and (51.9)!) the strain tensor may be replaced by the distortion tensor $\partial\boldsymbol{u}/\partial\boldsymbol{r}$ or by the transposed tensor Grad $\boldsymbol{u}$ (see Sec. 49). The point is that $\boldsymbol{\varepsilon} = \partial\boldsymbol{u}/\partial\boldsymbol{r} - \boldsymbol{\omega} = \text{Grad}\,\boldsymbol{u} + \boldsymbol{\omega}$, the tensor of small rotations $\boldsymbol{\omega}$ is antisymmetric, and in the contraction with tensor $\mathbf{c}$ symmetric with respect to the last pair of indices it yields zero: $c_{ijkl}\omega_{kl} = 0$, $\mathbf{c} : \boldsymbol{\omega} = 0$. Therefore Hooke's law (51.3) can be written thus:

$$\sigma_{ij} = c_{ijkl}\frac{\partial u_k}{\partial x_l}, \quad \boldsymbol{\sigma} = \mathbf{c} : \frac{\partial\boldsymbol{u}}{\partial\boldsymbol{r}} = \boldsymbol{c} : \text{Grad}\,\boldsymbol{u}. \tag{51.13}$$

Substituting these expressions into (50.7), we obtain the equations of motion of an elastic body (the equations of *elastodynamics*)

$$c_{ijkl}\frac{\partial^2 u_k}{\partial x_j\,\partial x_l} = \rho\frac{\partial^2 u_i}{\partial t^2}, \quad \mathbf{c}\,\vdots\,\text{Grad Grad}\,\boldsymbol{u} = \rho\frac{\partial^2\boldsymbol{u}}{\partial t^2}, \tag{51.14}$$

and substituting them into (50.8) we obtain the equations of elastic equilibrium (the equations of *elastostatics*)

$$c_{ijkl}\frac{\partial^2 u_k}{\partial x_j\,\partial x_l} = 0, \quad \mathbf{c}\,\vdots\,\text{Grad Grad}\,\boldsymbol{u} = 0. \tag{51.15}$$

This is a system of three linear partial differential equations of the second order in three unknowns. It can be conveniently used for the solution of problems of the theory of elasticity in cases when boundary conditions are specified for displacements. But the boundary

conditions are more often specified for stresses, i.e. when the forces applied to the crystal surface are given. We wish to note that boundary conditions on the parts of the crystal surface that are free of loads are specified exactly for stresses: the forces applied to these parts of the surface are zero, but the displacements here are, generally speaking, different from zero.

In specifying boundary conditions for stresses it is more convenient to write down the differential equations of the theory of elasticity so that the components of the stress tensor $\boldsymbol{\sigma}$ would be the unknown functions. They must, as we know, satisfy the Cauchy relations (50.8); the components of the strain tensor $\boldsymbol{\varepsilon}$ thus obtained with the aid of Hooke's law must satisfy Saint-Venant's compatibility equations (49.18). Thus we arrive at a system of nine differential equations in six unknown functions $\sigma_{ij}(\boldsymbol{r})$*:

$$\operatorname{Div}\boldsymbol{\sigma}=0, \quad \frac{\partial\sigma_{ij}}{\partial x_j}=0, \tag{51.16}$$

$$\operatorname{Inc}(\mathbf{s}:\boldsymbol{\sigma})=0, \quad \delta_{ikn}\delta_{jlm}s_{mnpq}\frac{\partial^2\sigma_{pq}}{\partial x_k\,\partial x_l}=0 \tag{51.17}$$

with three boundary conditions

$$\boldsymbol{\sigma}\cdot\boldsymbol{n}=\boldsymbol{P}, \quad \sigma_{ij}n_j=P_i, \tag{51.18}$$

where $\boldsymbol{P}$ is the vector function of coordinates specified for the whole surface of the elastic body. It can be proved** that this system always has a solution, and a unique one at that.

Hooke's law is written down here without temperature terms, therefore the derived equations describe the elastic equilibrium of a crystal at constant temperature. We shall discuss the thermal expansion of the crystal and the temperature stresses related to it in Sec. 55.

In solving stress equations of the theory of elasticity in sufficiently complicated cases the tensor of stress functions $\boldsymbol{\Phi}$ is generally used. This is a symmetric second-rank tensor related to the stress tensor $\boldsymbol{\sigma}$ by the relation $\boldsymbol{\sigma}=\operatorname{Inc}\boldsymbol{\Phi}$. It can be easily verified that $\operatorname{Div}\operatorname{Inc}=0$, so that the Cauchy relations of elastic equilibrium are identically satisfied, and to find $\boldsymbol{\Phi}$ it will suffice to solve the system of equations $\operatorname{Inc}(\mathbf{s}:\operatorname{Inc}\boldsymbol{\Phi})=0$ with boundary conditions $\boldsymbol{n}\cdot\operatorname{Inc}\boldsymbol{\Phi}=\boldsymbol{P}$. The stress function tensor is defined in this case not uniquely but only up to a term of Def $\boldsymbol{v}$ type, where $\boldsymbol{v}$ is an arbitrary vector. This ambiguity is unimportant, however, since it follows from Saint-Venant's compatibility that $\operatorname{Inc}\operatorname{Def}=0$. Thus, after all the stress tensor $\boldsymbol{\sigma}$ is determined quite uniquely. For details see Lurie (1955, Ch. I, Sec. 5) and Krutkov (1949). In general for the solution of problems of the anisotropic theory of elasticity refer to the works of Lekhnitsky (1947, 1950, 1971) and Ambartsumyan (1967). Special notice should be made of the problem of the construction of Green's tensor for a system of equations for the elastostatics of crystals (51.15)—see Lifshits and Rosenzweig (1947).

* In case of anisotropic bodies equations (51.7) are called the generalized equations of Beltrami-Mitchell.

** For proof see, e.g., Leibenson (1947, Sec. 118) or Novozhilov (1958, Ch. V, Sec. 18).

Sec. 52. Symmetry of the Elastic Properties of Crystals

In Sec. 51 there were introduced matter tensors **s**, **c**, α, and β that characterize the elastic properties, thermal expansion and thermoelasticity of crystals. Tensors α and β are symmetric second-rank tensors; the influence of crystal symmetry on the properties described by such tensors was discussed in detail in Ch. III. Figs. 24.1, 24.2, 24.3 show the representation surfaces of the thermal expansion of some crystals. As distinct from tensors of dielectric permittivity, thermal and electrical conductivity, the thermal expansion tensor can have negative eigenvalues too. Therefore the representation surfaces of the thermal expansion of some crystals, e.g., of calcite and ethylene diamine tartrate (cf. Figs. 24.3 and 52.1) are black and white* which is never the case with the representation surfaces of the earlier discussed matter tensors. The black parts of a representation surface correspond to those directions in a crystal in which the linear dimensions do not increase with temperature rise, as usually, but decrease. The cone of directions in which the thermal expansion is zero is determined by the equation $\alpha_{ij}q_iq_j = 0$ with respect to the components of a unit vector $\boldsymbol{q}$. For instance, for calcite this vector makes up an angle of 64°43′ with the principal symmetry axis X_3. The geometry of the thermal expansion of crystals was discussed in detail by A. V. Shubnikov (1956).

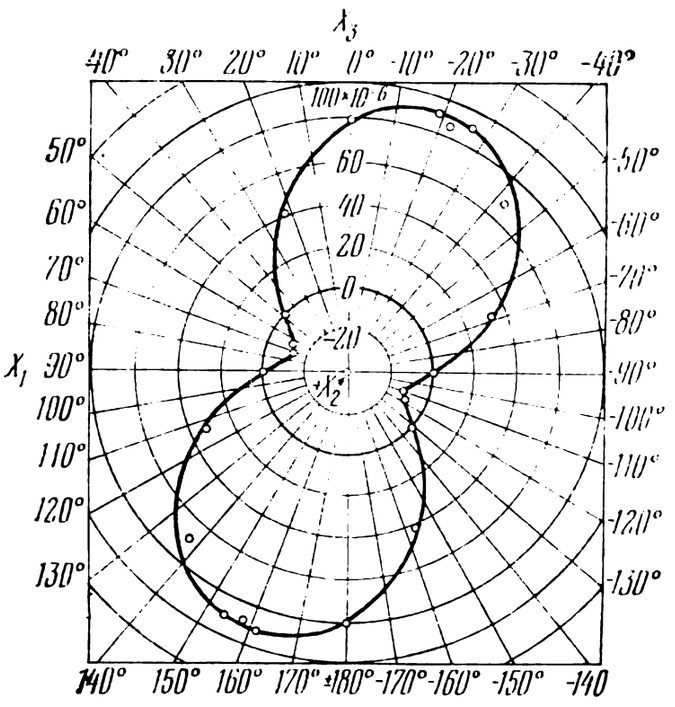


Fig. 52.1. Thermal expansion of a crystal of ethylene diamine tartrate, class 2, in plane X_1X_2 (this is not a section of the representation surface). (Mason, 1952)

The general form of the tensors of elasticity and elastic compliance coefficients invariant with respect to all the possible crystallographic and limit groups are given in Table E.18. It does not follow, however, from the differences in the general form of these tensors in some clas-

* In this and the following figures the positive "black" and negative "white" parts of the surfaces are marked with the plus and minus signs respectively.

ses that the symmetry of the elastic properties of the corresponding crystals is also different. Thus, it can be seen from Tables E.18 and 47.1 that the number of independent invariants in the elastic properties tensor is the same in both subsystems of the tetragonal system. The different number of independent components and the different forms of the tensors in the higher and lower subsystems can be simply explained by the fact that the directions of base vectors $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are not determined by the symmetry elements of crystals in the lower subsystems of the intermediate category. Therefore we shall introduce for the lower subsystem, along with the crystal-physical basis $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$, a basis

$$\begin{aligned} \boldsymbol{e}_1' &= \boldsymbol{e}_1 \cos\varphi + \boldsymbol{e}_2 \sin\varphi, \\ \boldsymbol{e}_2' &= -\boldsymbol{e}_1 \sin\varphi + \boldsymbol{e}_2 \cos\varphi, \\ \boldsymbol{e}_3' &= \boldsymbol{e}_3, \end{aligned} \tag{52.1}$$

having chosen the angle φ so that the component s_{16}' of tensor $s_{\lambda\mu}$ in this basis vanishes:

$$s_{16}' = P_{1'\lambda} P_{6'\mu} s_{\lambda\mu} = 0. \tag{52.2}$$

Substituting in (52.2) the elements of matrix $P_{\varkappa'\lambda}$ describing the rotation about the axis X_3 (see formula (F.26)) and the components of the tensor for the lower subsystem of the tetragonal system (see Table E.18), we find

$$\tan 4\varphi = \frac{4s_{16}}{2(s_{11} - s_{12}) - s_{66}}. \tag{52.3}$$

The angle φ can be found from the condition that the component c_{16}' of tensor $c_{\lambda\mu}$ vanishes. Thus we obtain

$$\tan 4\varphi = \frac{4c_{16}}{c_{11} - c_{12} - 2c_{66}}. \tag{52.4}$$

So, in the basis (52.1) where the angle φ is determined by condition (52.3) or (52.4), tensors **s** and **c** for the lower subsystem of the tetragonal system have the same form as the one which these tensors have in the crystal-physical basis for the higher subsystem of the same system. Hence it follows that all crystals of the tetragonal system constitute a single class $4/mmm$ of elastic symmetry. Figs. 54.3-54.5 show that the representation surfaces of the elastic properties of crystals of both subsystems of the tetragonal system really have one and the same symmetry $4/mmm$.

The two subsystems of the trigonal system also constitute one class $\bar{3}m$ of elastic symmetry. Basis (52.1) for the lower subsystem of the trigonal system is determined by the condition

$$\tan 3\varphi = \frac{s_{25}}{s_{14}} = \frac{c_{25}}{c_{14}}. \tag{52.5}$$

Although the general form of the elastic properties tensors was defined back in the 19th century, it has been noticed comparatively recently that the elastic symmetry classes $\bar{3}m$ and $4/mmm$ coincide with the trigonal and tetragonal systems.

Tensors **c** and **s**, as well as any others (see, e.g. Sec. 83), can be expanded into irreducible parts. These irreducible parts are expressed in terms of the irreducible tensors introduced in Sec. 47 with the aid of the Kronecker and Levi-Civita isotropic tensors. We shall expand tensors **c** and **s** in two stages. At the first stage we eliminate the parts $\mathbf{c}^{\{4\}}$ and $\mathbf{s}^{(4)}$ that are symmetric with respect to all indices; the remaining parts $\mathbf{c}^{\{22\}}$ and $\mathbf{s}^{\{22\}}$ with internal symmetry $[[V^2]^2]$ (see Sec. 42) vanish when being symmetrized for all indices. Thus, the first stage of the expansion is:

$$\mathbf{s} = \mathbf{s}^{\{4\}} + \mathbf{s}^{\{22\}}, \quad s^{\{4\}}_{ijkl} = s_{(ijkl)}, \quad s^{\{22\}}_{ijkl} = s_{ijkl} - s_{(ijkl)}. \tag{52.6}$$

(the formulas for **c** are perfectly similar). Using the methods of the theory of group representation it can be shown that $\mathbf{s}^{\{4\}}$ is expanded into scalar, deviator and nonor parts, while $\mathbf{s}^{\{22\}}$ into scalar and deviator parts. The internal symmetry of tensors $\mathbf{s}^{\{4\}}$ and $\mathbf{s}^{\{22\}}$ unambiguously (up to numerical coefficients) determines the expansions at the second stage*:

$$s^{\{4\}}_{ijkl} = I^{\{4\}}\delta_{(ij}\delta_{kl)} + D^{\{4\}}_{(ij}\delta_{kl)} + N^{\{4\}}_{ijkl}, \tag{52.7}$$

$$s^{\{22\}}_{ijkl} = I^{\{22\}}(\delta_{ij}\delta_{kl} - \delta_{(ij}\delta_{kl)}) + \\ + \left[\frac{1}{2}(D^{\{22\}}_{ij}\delta_{kl} + D^{\{22\}}_{kl}\delta_{ij}) - D^{\{22\}}_{(ij}\delta_{kl)}\right]. \tag{52.8}$$

By the convolution of the right- and left-hand sides of these equalities we shall easily find the expressions for irreducible tensors $I^{\{4\}}$, $\mathbf{D}^{\{4\}}, \ldots$ $\ldots$, $\mathbf{D}^{\{22\}}$ in terms of tensors $\mathbf{s}^{\{4\}}$ and $\mathbf{s}^{\{22\}}$:

$$I^{\{4\}} = \frac{1}{5}s^{\{4\}}_{iikk}, \quad D^{\{4\}}_{ij} = \frac{2}{7}(3s^{\{4\}}_{ijkk} - 5I^{\{4\}}\delta_{ij}),$$

$$N^{\{4\}}_{ijkl} = s^{\{4\}}_{ijkl} - I^{\{4\}}\delta_{(ij}\delta_{kl)} - D^{\{4\}}_{(ij}\delta_{kl)};$$

$$I^{\{22\}} = \frac{1}{4}s^{\{22\}}_{iikk}, \quad D^{\{22\}}_{ij} = 3s^{\{22\}}_{ijkk} - 4I^{\{22\}}\delta_{ij}.$$

---

* The first stage consists in the expansion of tensors **c** and **s** into parts transforming according to the irreducible representations of the group of all the possible linear transformations of the three-dimensional space GL (3); here {4} and {22} are the notation of the corresponding irreducible representations. At the second stage each of them is expanded, in its turn, into parts transforming according to the irreducible representations D_l of the orthogonal group $\infty\infty m$ or O (3), so they are called the irreducible parts. For more details see Sirotin (1974); the same source also contains formulas for the expansion of other matter tensors into irreducible parts.

For crystals of the classes in which the irreducible deviators and nonors are multiples of the unit ones, i.e. $D^{\{4\}}_{(ij)} = S^{\{4\}}_D D^{(0)}_{ij}$, $D^{\{22\}}_{ij} = S^{\{22\}}_D D^{(0)}_{ij}$, etc. (see Table 47.4), these expansions are essentially simplified and become

$$\begin{aligned} s_{ijkl} = {} & S^{\{4\}}_I \delta_{(ij}\delta_{kl)} + S^{\{4\}}_D D^0_{(ij}\delta_{kl)} + S^{\{4\}}_N N^0_{ijkl} + \\ & + S^{\{22\}}_I (\delta_{ij}\delta_{kl} - \delta_{(ij}\delta_{kl)}) + \\ & + S^{\{22\}}_D \left[\frac{1}{2} (D^0_{ij}\delta_{kl} + D^0_{kl}\delta_{ij}) - D^0_{(ij}\delta_{kl)} \right] = \\ & = \frac{1}{3} (S^{\{4\}}_I + 2S^{\{22\}}_I)\, \delta_{ij}\delta_{kl} + \\ & + \frac{1}{3} (S^{\{4\}}_I - S^{\{22\}}_I)\, (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \\ & + \frac{1}{6} (S^{\{4\}}_D + 2S^{\{22\}}_D)\, (D^0_{ij}\delta_{kl} + D^0_{kl}\delta_{ij}) + \\ & + \frac{1}{6} (S^{\{4\}}_D - S^{\{22\}}_D)\, (D^0_{ik}\delta_{jl} + D^0_{jl}\delta_{ik} + \\ & \qquad + D^0_{il}\delta_{jk} + D^0_{jk}\delta_{il}) + S^{\{4\}}_N N^0_{ijkl}. \end{aligned} \tag{52.9}$$

Here the coefficients $S^{\{4\}}_I \equiv I^{\{4\}}$ and $S^{\{22\}}_I \equiv I^{\{22\}}$ are introduced for the uniformity of notation. Expansions (52.7) and (52.8) are combined, but with the aid of indices $\{4\}$ and $\{22\}$ of the coefficients S they are easily separated.

In accordance with Hermann's theorem (see Sec. 46), the crystals of the hexagonal system are transversally isotropic in their elastic properties and together with textures constitute the elastic symmetry class ∞/mm. All the directions which make up one and the same angle with the principal symmetry axis are equal in their elastic properties, although for the hexagonal crystals these directions are certainly crystallographically different. This is one of the numerous cases when the symmetry of a crystal property is higher than the symmetry of the crystal itself.

In crystals of the hexagonal system and in textures the deviators and nonors are multiples of the unit ones, the unit deviator and nonor being specified by the formulas

$$D^0_{ij} = \frac{1}{2} (3k_i k_j - \delta_{ij}), \tag{52.10}$$

$$N^0_{ijlm} = \frac{1}{8} (35k_i k_j k_l k_m - 30k_{(i}k_j\delta_{lm)} + 3\delta_{(ij}\delta_{lm)}), \tag{52.11}$$

where $\boldsymbol{k}$ is the unit vector of the principal symmetry axis; in the crystal-physical system of coordinates $k_i = \delta_{i3}$, and formulas (52.10) and (52.11) transform into formulas for $\mathbf{D}^0\,[\infty/mm]$ and $\mathbf{N}^0\,[\infty/(mm)]$ from Table 47.4.

For these crystals the coefficients of expansion (52.9) are

$$
\begin{aligned}
S_I^{\{4\}} &= \frac{1}{15}(8s_{11}+3s_{33}+4s_{13}+2s_{44}),\\
S_I^{\{22\}} &= \frac{1}{6}(-s_{11}+3s_{12}+4s_{13}-s_{44}),\\
S_D^{\{4\}} &= \frac{2}{21}(-8s_{11}+6s_{33}+2s_{13}+s_{44}),\\
S_D^{\{22\}} &= \frac{1}{3}(2s_{11}-6s_{12}+4s_{13}-s_{44}),\\
S_N^{\{4\}} &= \frac{8}{35}(s_{11}+s_{33}-2s_{13}-s_{44}).
\end{aligned}
\tag{52.12}
$$

Tensor **c** is expanded in the same way. In applying (52.9) to tensor **c** the coefficients should be naturally denoted $C_I^{\{4\}}, \ldots, C_D^{\{22\}}$. These coefficients are computed with the aid of (52.12) where $s_{11}, \ldots, s_{13}$ are replaced by $c_{11}, \ldots, c_{13}$ and $4c_{44}$ should be substituted for s_{44}.

If the coefficients $C_D^{\{4\}}$, $C_D^{\{22\}}$ and $C_N^{\{4\}}$ or $S_D^{\{4\}}$, $S_D^{\{22\}}$ and $S_N^{\{4\}}$ vanish, tensors of elasticity coefficients and of elastic compliance coefficients would be isotropic. Hence it is clear that these sets of coefficients are characteristic of the anisotropy of bodies transversally isotropic in their elastic properties. It can readily be seen that the vanishing of all the coefficients of one set involves turning to zero of all the coefficients of the other set. On the other hand, coefficients $C_I^{\{22\}}$ and $C_D^{\{22\}}$ and correspondingly $S_I^{\{22\}}$ and $S_D^{\{22\}}$ characterize the non-symmetry of tensors **c** and **s** with respect to indices: if they vanish, the internal symmetry of tensors **c** and **s** would be $[V^4]$.

As regards the symmetry of their elastic properties crystals of the cubic system differ from the isotropic bodies and constitute the elastic symmetry class $m3m$. Nonors for them are multiples of the unit one, while deviators become zero (see Table 47.1). Therefore expansion (52.9) for the cubic crystals is still more simplified and becomes

$$
\begin{aligned}
s_{ijkl} &= S_I^{\{4\}}\delta_{(ij}\delta_{kl)} + S_N^{\{4\}}N_{ijkl}^0 + S_I^{\{22\}}(\delta_{ij}\delta_{kl}-\delta_{(ij}\delta_{kl)}) =\\
&= \frac{1}{3}(S_I^{\{4\}}+2S_I^{\{22\}})\,\delta_{ij}\delta_{kl} +\\
&+ \frac{1}{3}(S_I^{\{4\}}-S_I^{\{22\}})(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) + S_N^{\{4\}}N_{ijkl}^0.
\end{aligned}
\tag{52.13}
$$

The unit nonor of the cubic symmetry (it should be denoted by $\mathbf{N}^0$ $[m3m]$ to distinguish it from $\mathbf{N}^0$ $[\infty/mm]$ introduced above), in accordance with Sec. 47, has the following components in the crystal-

physical system of coordinates

$$N^0_{ijkl} = \begin{cases} 1 & \text{for four equal indices,} \\ -1/2 & \text{for two pairs of equal indices,} \\ 0 & \text{in all other cases.} \end{cases} \quad (52.14)$$

The coefficients of expansion (52.13) are computed from formulas

$$S_I^{\{4\}} = \frac{1}{5}(3s_{11} + 2s_{12} + s_{44}),$$

$$S_I^{\{22\}} = s_{12} - \frac{1}{4} s_{44}, \quad (52.15)$$

$$S_N^{\{4\}} = \frac{1}{5}(2s_{11} - 2s_{12} - s_{44}).$$

The tensor of the elasticity coefficients is also defined by formula (52.13) where the coefficients C replace the coefficients S; the former are computed from formulas (52.15) in which instead of s_{11}, s_{12} and s_{44} there are substituted c_{11}, c_{12}, and $4c_{44}$ respectively.

The non-symmetry of tensors **c** and **s** with respect to indices is characterized by coefficients $C_I^{\{22\}}$ and $S_I^{\{22\}}$ respectively. The elastic anisotropy of cubic crystals is determined by coefficients $C_N^{\{4\}}$ and $S_N^{\{4\}}$; when one of them is zero, the other one is also zero. Since the elastic constants essentially depend on temperature, the elastic anisotropy coefficients also depend on temperature. Thus the elastic anisotropy of rock salt decreases with the rise of temperature up to 690 K, when the crystal becomes elastically isotropic, and with further increase in temperature the sign of the elastic anisotropy (i.e. of coefficients $C_N^{\{4\}}$ and $S_N^{\{4\}}$) changes. The degree of elastic anisotropy is measured by a dimensionless ratio

$$A = \frac{2c_{44}}{c_{11} - c_{12}} = \frac{2(s_{11} - s_{12})}{s_{44}}, \quad (52.16)$$

which characterizes the dependence of the resistance of a cubic crystal to shear strain on direction (see table (53.3)).

In isotropic and gyrotropic bodies the coefficients of elasticity and elastic compliance are isotropic:

$$s_{ijkl} = S_I^{\{4\}}\delta_{(ij}\delta_{kl)} + S_I^{\{22\}}(\delta_{ij}\delta_{kl} - \delta_{(ij}\delta_{kl)}) =$$

$$= \frac{1}{3}(S_I^{\{4\}} + 2S_I^{\{22\}})\,\delta_{ij}\delta_{kl} +$$

$$+ \frac{1}{3}(S_I^{\{4\}} - S_I^{\{22\}})(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \quad (52.17)$$

$$S_I^{\{4\}} = s_{11}, \quad S_I^{\{22\}} = \frac{1}{2}(s_{11} - 3s_{12}), \quad (52.18)$$

Similar formulas hold for tensor **c**. For isotropic bodies from formulas (52.11) there follow relations*

$$(c_{11} - c_{12})(s_{11} - s_{12}) = (c_{11} + 2c_{12})(s_{11} + 2s_{12}) = c_{44}s_{44} = 1, \quad (52.19)$$

and from (52.16) relations

$$c_{11} - c_{12} = 2c_{44}, \quad 2(s_{11} - s_{12}) = s_{44}. \quad (52.20)$$

For the characteristics of elastic properties of isotropic bodies there are used, along with coefficients of elasticity and elastic compliance coefficients, also Young's modulus, $E = 1/s_{11}$, Poisson's ratio, $\nu = -s_{12}/s_{11}$, bulk modulus, $K = (c_{11} + 2c_{12})/3$, shear modulus, $G = (c_{11} - c_{12})/2 = 1/s_{44}$, and Lamé's coefficients, $\lambda = c_{12}$ and $\mu = G$. Two independent coefficients fully characterize the elastic properties of isotropic material. In general, for the elastic properties of crystals see Alexandrov and Ryzhova (1961); Musgrave (1970); Auld (1973); Dieulesaint, and Royer (1974); Krishnan (1958); Krishnan, Radha, Gopal (1971).

Sec. 53. Simple States of Stress

By simple states of stress we shall mean such states at which the stress tensor σ depends linearly on the Cartesian coordinates

$$\sigma = \mathbf{A} + \mathbf{B}\cdot\mathbf{r}, \quad \sigma_{ij} = A_{ij} + B_{ijk}x_k, \quad (53.1)$$

Here **A** and **B** are tensors independent of the coordinates: **A** is a symmetric second-rank tensor, **B** is a third-rank tensor symmetric with respect to the first two indices. The following theorem is valid.

Theorem of Simple States of Stress. If under the action of some forces on an isotropic body there develops a simple state of stress applied to the body surface, then the same state of stress will develop in an anisotropic body of the same shape and under the action of the same forces.

The proof is based on the theorem on the unique solution of equations pertaining to the theory of elasticity. Indeed, the Beltrami-Michell equations (see Sec. 51) contain only the second derivatives of the stress tensor which, at a simple state of stress are all equal to zero, so that these equations are identically satisfied. The Cauchy relations of elastic equilibrium (see Sec. 50) contain no characteristics of a material at all, so that in replacing one body by another (of the same shape and under the same boundary conditions) the equations do not change. Thus one and the same simple state of stress is the solution of the stress equations of the theory of elasticity for all the possible *homogeneous* (this is essential!) elastic bodies. By virtue of the theorem of uniqueness there can be no other solution for any of these bodies.

* Formulas (52.19) also hold for crystals of the cubic system.

In this and in the following sections we shall discuss some of the practically important examples of the use of the theorem proved.

We shall begin with cases of a homogeneous stress field, i.e. when the stress tensor is independent of the coordinates. The Cauchy equations are identically satisfied here, therefore it will suffice to verify only that the boundary conditions are satisfied.

Uniform Compression. If hydrostatic pressure p acts on an elastic body, the boundary conditions are as follows

$$\boldsymbol{\sigma}\cdot\boldsymbol{n} = -p\boldsymbol{n}, \quad \sigma_{ij}n_j = -pn_i; \tag{53.2}$$

$\boldsymbol{n}$ is the unit vector of an external normal to the surface. (In case of a uniform extension by force $p\boldsymbol{n}$ the signs are reversed). An apparent solution

$$\boldsymbol{\sigma} = -p\mathbf{I}, \quad \sigma_{ij} = -p\delta_{ij} \tag{53.3}$$

satisfies all the equations and the boundary conditions. Thus the stress is entirely independent of the elastic characteristics of the body. A strain

$$\boldsymbol{\varepsilon} = -p\mathbf{s}:\mathbf{I}, \quad \varepsilon_{ij} = -ps_{ijkk} \tag{53.4}$$

however, essentially depends on them. A symmetric second-rank tensor, $S_{ij} = s_{ijkk}$, is called *the tensor of the compressibility coefficients.* With its aid the strain under hydrostatic pressure is written as

$$\varepsilon_{ij} = -S_{ij}p, \quad \varepsilon_\lambda = -S_\lambda p. \tag{53.5}$$

The formulas expressing the components S_{ij} of tensor $\mathbf{S}$ in terms of the elastic compliance coefficients, $s_{\lambda\mu}$, for all crystallographic classes are given in Table 53.1. Among other features it can be seen from the Table, that the influence of the symmetry of crystals on their strain at a hydrostatic pressure is the same as on all the other crystal properties described by symmetric second-rank tensors (dielectric permittivity, thermal expansion, etc.).

The relative change in volume under hydrostatic pressure $\Delta V/V = \varepsilon_{ii} = -S_{iip}$ is characterized by the scalar $K^{-1} = S_{ii} = S_{iikk}$ which is *the coefficient of uniform (cubic) extension.* The quantity K, reciprocal of it, is called *the modulus of uniform extension.* The change of the shape of elastic anisotropic bodies under hydrostatic pressure is characterized by the strain deviator, $e_{ij} = -R_{ij}p$, proportional to the deviator of the compressibility coefficients tensor:

$$R_{ij} = S_{ij} - \frac{1}{3}K^{-1}\delta_{ij}. \tag{53.6}$$

Uniaxial Extension. Let us consider a cylindrical rod with an arbitrary cross-section of area S, to the ends of which tensile forces $S\sigma$ are applied, distributed uniformly over the end surfaces; the lateral surface of the rod is free of loads. Let us denote by q a unit

Table 53.1

Tensor $S_{ij}=s_{ijkk}$ for All Crystallographic and Limit Classes

Systems	Tensor $S_{ij}=s_{ijkk}$		
Triclinic	$s_{11}+s_{31}+s_{12}$ $1/2\,(s_{16}+s_{26}+s_{36})$ $1/2\,(s_{15}+s_{25}+s_{35})$	$1/2\,(s_{16}+s_{26}+s_{36})$ $s_{22}+s_{12}+s_{23}$ $1/2\,(s_{14}+s_{24}+s_{34})$	$1/2\,(s_{15}+s_{25}+s_{35})$ $1/2\,(s_{14}+s_{24}+s_{34})$ $s_{33}+s_{23}+s_{31}$
Monoclinic $2 \parallel X_2$ $2 \parallel X_3$	$s_{11}+s_{31}+s_{12}$ 0 $1/2\,(s_{15}+s_{25}+s_{35})$ $s_{11}+s_{31}+s_{12}$ $1/2\,(s_{16}+s_{26}+s_{36})$ 0	0 $s_{22}+s_{12}+s_{23}$ 0 $1/2\,(s_{16}+s_{26}+s_{36})$ $s_{22}+s_{12}+s_{23}$ 0	$1/2\,(s_{15}+s_{25}+s_{35})$ 0 $s_{33}+s_{23}+s_{31}$ 0 0 $s_{33}+s_{23}+s_{31}$
Rhombic	$s_{11}+s_{31}+s_{12}$ 0 0	0 $s_{22}+s_{12}+s_{23}$ 0	0 0 $s_{33}+s_{23}+s_{31}$
Trigonal, tetragonal, hexagonal, and textures	$s_{11}+s_{12}+s_{13}$ 0 0	0 $s_{22}+s_{12}+s_{13}$ 0	0 0 $s_{33}+2s_{13}$
Cubic system and isotropic bodies	$s_{11}+2s_{12}$ 0 0	0 $s_{11}+2s_{12}$ 0	0 0 $s_{11}+2s_{12}$

vector directed along the rod axis. The stress tensor

$$\sigma=\sigma \boldsymbol{qq}, \quad \sigma_{ij}=\sigma q_i q_j, \tag{53.7}$$

evidently satisfies boundary conditions. Hence, according to Hooke's law we determine the strains

$$\varepsilon=\sigma \mathrm{s}:\boldsymbol{qq}, \quad \varepsilon_{ij}=\sigma s_{ijkl} q_k q_l. \tag{53.8}$$

The relative elongation of the rod $\Delta l/l = \varepsilon_{ij} q_i q_j = \sigma s_{ijkl} q_i q_j q_k q_l$. Its ratio to stress σ is the reciprocal quantity of *Young's modulus* E for direction $\boldsymbol{q}$:

$$E^{-1}(\boldsymbol{q})=s_{ijkl} q_i q_j q_k q_l=\boldsymbol{qq}:\mathrm{s}:\boldsymbol{qq}. \tag{53.9}$$

Table 53.2

The Young Moduius Reciprocal $E^{-1}(q)=E^{-1}[hkl]$ Expressed in Terms of the Components q_i of the Unit Vector q and Miller Indices $h^i=h,\ k,\ l$ of the Crystallographic Direction $[hkl]\parallel q$

General formulas

$$E^{-1}=s_{\lambda\mu}Q_\lambda Q_\mu,\quad \text{where}\quad Q_\lambda=q_iq_j=\frac{A_{\alpha i}A_{\beta j}h^\alpha h^\beta}{g_{\gamma\eta}h^\gamma h^\eta}\quad (il\leftrightarrow\lambda=1,\ldots,6)$$

Triclinic system

$$\begin{aligned}E^{-1}=&\,s_{11}Q_1^2+s_{22}Q_2^2+s_{33}Q_3^2+(s_{44}+2s_{23})\,Q_2Q_3+\\&+(s_{55}+2s_{31})\,Q_3Q_1+(s_{66}+2s_{12})\,Q_1Q_2+2\,(s_{14}+s_{56})\,Q_1Q_4+\\&+2\,(s_{25}+s_{64})\,Q_2Q_5+2\,(s_{36}+s_{45})\,Q_3Q_6+2s_{15}Q_1Q_5+\\&+2s_{16}Q_1Q_6+2s_{26}Q_2Q_6+2s_{24}Q_2Q_4+2s_{34}Q_3Q_4+2s_{35}Q_3Q_5,\end{aligned}$$

where

$$\begin{aligned}Q_1&=q_1^2=(ha\sin\beta-kb\sin\alpha\cos\gamma^*)^2/g,\\Q_2&=q_2^2=(k/b^*)^2/g,\\Q_3&=q_3^2=(ha\cos\beta+kb\cos\alpha+lc)^2/g,\\Q_4&=q_2q_3=(k/b^*)\,(ha\cos\beta+kb\cos\alpha+lc)/g,\\Q_5&=q_3q_1=(ha\cos\beta+kb\cos\alpha+lc)\,(ha\sin\beta-kb\sin\alpha\cos\gamma^*)/g,\\Q_6&=q_1q_2=(k/b^*)\,(ha\sin\beta-kb\sin\alpha\cos\gamma^*)/g,\\g&=h^2a^2+k^2b^2+l^2c^2+2klbc\cos\alpha+2lhca\cos\beta+2hkab\cos\gamma.\end{aligned}$$

Monoclinic system ($2\parallel X_2,\ m\perp X_2$)

$$\begin{aligned}E^{-1}=&\,s_{11}Q_1^2+s_{22}Q_2^2+s_{33}Q_3^2+(s_{44}+2s_{23})\,Q_2Q_3+(s_{55}+2s_{31})\,Q_3Q_1+\\&+(s_{66}+2s_{12})\,Q_1Q_2+2\,(s_{25}+s_{64})\,Q_2Q_5+2s_{15}Q_1Q_5+2s_{35}Q_3Q_5,\end{aligned}$$

where

$$\begin{aligned}&Q_1=q_1^2=(ha\sin\beta)^2/g,\quad Q_3=q_3^2=(ha\cos\beta+lc)^2/g,\\&Q_2=q_2^2=(kb)^2/g,\qquad Q_5=q_3q_1=ha\sin\beta\,(ha\cos\beta+lc)/g,\\&g=h^2a^2+k^2b^2+l^2c^2+2lhca\cos\beta.\end{aligned}$$

Rhombic system

$$\begin{aligned}E^{-1}=&\,s_{11}q_1^4+s_{22}q_2^4+s_{33}q_3^4+(s_{44}+2s_{23})\,q_2^2q_3^2+\\&+(s_{55}+2s_{31})\,q_3^2q_1^2+(s_{66}+2s_{12})\,q_1^2q_2^2=\\=&\,[h^4a^4s_{11}+k^4b^4s_{22}+l^4c^4s_{33}+k^2l^2b^2c^2\,(s_{44}+2s_{23})+l^2h^2c^2a^2\,(s_{55}+2s_{31})\\&+h^2k^2a^2b^2\,(s_{66}+2s_{12})]/(h^2a^2+k^2b^2+l^2c^2)^2.\end{aligned}$$

Tetragonal system

$$\begin{aligned}E^{-1}=&\,s_{11}(q_1^4+q_2^4)+s_{33}q_3^4+(s_{44}+2s_{13})\,(q_1^2+q_2^2)q_3^2+\\&+(s_{66}+2s_{12})\,q_1^2q_2^2+2s_{16}q_1q_2\,(q_1^2-q_2^2)=\\=&\,\{a^4\,[(h^4+k^4)\,s_{11}+h^2k^2\,(s_{66}+2s_{12})+2hk\,(h^2-k^2)\,s_{16}]+\\&+l^4c^4s_{33}+(h^2+k^2)\,l^2a^2c^2\,(s_{44}+2s_{13})\}/[(h^2+k^2)\,a^2+l^2c^2]^2;\end{aligned}$$

for classes 4, $\bar{4}$, $4/m$ all the coefficients $s_{\lambda\mu}$ are different from zero; for classes 422, $4mm$, $42m$, $4/mmm$ the coefficient $s_{16}=0$.

Table 53.2 (cont'd)

Trigonal and hexagonal systems (at hexagonal orientation) and textures
$E^{-1} = s_{11}(1-q_3^2)^2 + s_{33}q_3^4 + (s_{44}+2s_{13})q_3^2(1-q_3^2) + 2s_{14}(3q_1^2-q_2^2)q_2q_3 + 2s_{25}(3q_2^2-q_1^2)q_1q_3 = \{(h^2+k^2-hk)^2a^4s_{11} + l^4c^4s_{33} + (h^2+k^2-hk)l^2a^2c^2(s_{44}+2s_{13}) + a^3c[3\sqrt{3}\,hkl(h-k)s_{14} + l(2h-k)(2k^2-h^2+hk)s_{25}]\} : [(h^2+k^2-hk)a^2+l^2c^2]^2;$
classes 3, $\bar{3}$—all the coefficients $s_{\lambda\mu}$ differ from zero; classes 32, $3m$, $\bar{3}m$—the coefficient $s_{25}=0$; the hexagonal system and textures—the coefficients $s_{14}=s_{25}=0$.
Cubic system
$E^{-1} = s_{11} - (2s_{11}-2s_{12}-s_{44})(q_2^2q_3^2+q_3^2q_1^2+q_1^2q_2^2) = s_{11} - (2s_{11}-2s_{12}-s_{44})(k^2l^2+l^2h^2+h^2k^2)/(h^2+k^2+l^2)^2$
Isotropic bodies
$E^{-1} = s_{11}$
Notation: $s_{\lambda\mu}$—coefficients of elastic compliance, a, b, c, α, β—parameters of crystal lattice, b^*, γ^*—parameters of reciprocal lattice; for $A_{\alpha i}$, $g_{\gamma\eta}$—see Appendix B.

The computation of Young's modulus can be simplified: if we introduce the notation $q_iq_j = (qq)_\lambda$, where $ij \leftrightarrow \lambda = 1, \ldots, 6$, then the stress components will be $\sigma_\mu = \sigma(qq)_\mu$, the strain components $\varepsilon_\lambda = \sigma s_{\lambda\mu}(qq)_\mu$ and, finally, Young's modulus reciprocal

$$E^{-1}(q) = s_{\lambda\mu}(qq)_\lambda(qq)_\mu. \tag{53.10}$$

This formula is more convenient than (53.9), it has considerably less terms while the values of $s_{\lambda\mu}$ are taken directly from the experimental data.

Formulas for the computation of Young's modulus are assembled in Table 53.2.

The relative change of the rod thickness, or, more exactly, of its linear dimensions in the direction $\boldsymbol{m}$ perpendicular to the direction of extension, is $\Delta l(\boldsymbol{m})/l(\boldsymbol{m}) = \varepsilon_{ij}m_im_j$. Let us express the strain in terms of stress; then $\Delta l(\boldsymbol{m})/l(\boldsymbol{m}) = \sigma s_{ijkl}m_im_jq_kq_l$. In the theory of elasticity of isotropic bodies the ratio of the change of the rod thickness to its length, taken with an opposite sign is called *Poisson's ratio* and is denoted by ν. If this notion is generalized for anisotropic bodies, Poisson's ratio will be a function of two mutually

perpendicular directions, $\boldsymbol{q}$ and $\boldsymbol{m}$:

$$\nu(\boldsymbol{q}, \boldsymbol{m}) = -\frac{\Delta l(\boldsymbol{m})/l(\boldsymbol{m})}{\Delta l(\boldsymbol{q})/l(\boldsymbol{q})} = -\frac{s_{ijkl}m_i m_j q_k q_l}{s_{nprt}q_n q_p q_r q_t} = -\frac{\boldsymbol{mm} : \boldsymbol{s} : \boldsymbol{qq}}{\boldsymbol{qq} : \boldsymbol{s} : \boldsymbol{qq}}. \quad (53.11)$$

The form more convenient for computations is this:

$$\nu(\boldsymbol{q}, \boldsymbol{m}) = -\frac{s_{\lambda\mu}(\boldsymbol{mm})_\lambda (\boldsymbol{qq})_\mu}{s_{\rho\sigma}(\boldsymbol{qq})_\rho (\boldsymbol{qq})_\sigma}. \quad (53.12)$$

Poisson's ratio of an anisotropic elastic medium can be so defined that it depends not on two unit vectors, but only on one vector, if it is interpreted as a characteristic of the change of areas in planes perpendicular to the direction of extension:

$$\nu = -\frac{\Delta S(\boldsymbol{q})/S(\boldsymbol{q})}{2\Delta l(\boldsymbol{q})/l(\boldsymbol{q})}. \quad (53.13)$$

Since $\Delta S(\boldsymbol{q})/S(\boldsymbol{q}) = \boldsymbol{\varepsilon} : (\mathbf{I} - \boldsymbol{qq}) = \varepsilon_{ij}(\delta_{ij} - q_i q_j)$, and the strain is computed with the aid of (53.8),

$$\nu(\boldsymbol{q}) = -\frac{\boldsymbol{qq} : \mathbf{s}(\mathbf{I} - \boldsymbol{qq})}{2\boldsymbol{qq} : \mathbf{s} : \boldsymbol{qq}} = -\frac{s_{ijkl}q_i q_j(\delta_{kl} - q_k q_l)}{2s_{nprt}q_n q_p q_r q_t}. \quad (53.14)$$

Noting that $(\boldsymbol{qq} : \mathbf{s} : \boldsymbol{qq})^{-1}$ is Young's modulus $E(\boldsymbol{q})$, and $\boldsymbol{qq} : \mathbf{s} : \mathbf{I} = \boldsymbol{q}\cdot\mathbf{S}\cdot\boldsymbol{q}$ is the normal component of the tensor of compressibility coefficients $\mathbf{S}$ in direction $\boldsymbol{q}$, we obtain one more definition for Poisson's ratio for anisotropic elastic media:

$$\nu(\boldsymbol{q}) = \frac{1}{2}[1 - \boldsymbol{q}\cdot\mathbf{S}\cdot\boldsymbol{q}E(\boldsymbol{q})]. \quad (53.15)$$

Under uniaxial extension the rod volume changes (it usually increases). The relative change of the volume $\Delta V/V = \varepsilon_{ii}$ in this case is

$$\Delta V/V = \sigma S_{ij}q_i q_j = \sigma\boldsymbol{q}\cdot\mathbf{S}\cdot\boldsymbol{q}, \quad (53.16)$$

where $\mathbf{S}$ is the tensor of compressibility coefficients. Comparing this result with formula (53.15) for Poisson's ratio $\nu(\boldsymbol{q})$ we see that the well-known formula $\Delta V/V = (1 - 2\nu)\sigma/E$ that defines the relative change of volume under uniaxial extension of isotropic bodies holds also for anisotropic bodies in the form

$$\frac{\Delta V}{V} = \frac{1 - 2\nu(\boldsymbol{q})}{E(\boldsymbol{q})}\sigma. \quad (53.17)$$

Poisson's ratios $\nu(\boldsymbol{q}, \boldsymbol{m})$ and $\nu(\boldsymbol{q})$ convince us once more that one and the same quantity characterizing a property of an isotropic body can be generalized in different ways for anisotropic bodies, and the choice of one or another generalization depends on the particular property of the anisotropic body we wish to describe.

Shear. Let tangential uniformly distributed forces be applied to the side faces of a rectangular rod; under this set of forces the rod

Table 53.3

Shear Modulus $G(n, l)$ for Glide Systems of Some Crystals

Glide system	Reciprocal value of shear modulus $G^{-1}(n, l)$	Crystals
	Triclinic system	
(100) [001]	$s_{44}\cos^2\gamma^* + s_{55}\sin^2\gamma^* + 2s_{45}\sin\gamma^*\cos\gamma^*$	kyanite
	Monoclinic system	
(010) [001]	s_{44}	gypsum
	Rhombic system	
(010) [100]	s_{66}	aragonite ($CaCO_3$)
(010) [001]	s_{44}	antimonite
	Trigonal system, classes 32, $3m$, $\bar{3}m$	
$(111)\,[01\bar{1}] = (0001)\,[\bar{1}2\bar{1}0]$	$\dfrac{8c^2(s_{11}-s_{12}) + 3a^2s_{44} - 8ac\sqrt{3}s_{14}}{3a^2+4c^2}$	Bi, calcite
$(100)\,[01\bar{1}] = (10\bar{1}1)\,[\bar{1}2\bar{1}0]$		calcite ($CaCO_3$)
	Tetragonal system, classes 422, $4mm$, $42m$, $4/mmm$	
(100) [001]	s_{44}	β-Sn
(110) [011]	s_{44}	β-Sn
$(1\bar{1}0)\,[111]$	$\dfrac{4a^2(s_{11}-s_{12}) + c^2s_{44}}{2a^2+c^2}$	β-Sn, $NH_4H_2PO_4$ (ADP)
$(101)\,[10\bar{1}]$	$\dfrac{4a^2c^2(s_{11}+s_{33}-2s_{13}) + (a^2-c^2)^2s_{44}}{(a^2+c^2)^2}$	β-Sn

$(11\bar{2})\ [111]$	$\dfrac{2a^2c^2(2s_{11}+4s_{33}+s_{66}+2s_{12}-8s_{13})+(2a^2-c^2)s_{44}}{(2a^2+c^2)^2}$	$NH_4H_2PO_4$ (ADP)
$(121)\ [10\bar{1}]$	$\dfrac{4a^2c^2(s_{11}+s_{33}+s_{66}-2s_{13})+(a^2+5c^2-2a^2c^2)s_{44}}{(a^2+c^2)(a^2+5c^2)}$	β-Sn
	Hexagonal system	
$(0001)\ [11\bar{2}0]$	s_{44}	Zn, Cd, Mg, Ti, Be, Co
$(01\bar{1}0)\ [\bar{2}110]$	$2(s_{11}-s_{12})$	Zn, Cd, Mg, Ti, Be
$(01\bar{1}1)\ [\bar{2}110]$	$\dfrac{8c^2(s_{11}-s_{12})+3a^2s_{44}}{3a^2+4c^2}$	Ti
$(1\bar{2}12)\ [10\bar{1}0]$	$\dfrac{2c^2(s_{11}-s_{12})+a^2s_{44}}{a^2+c^2}$	Mg
$(\bar{1}\bar{1}22)\ [11\bar{2}3]$	$\dfrac{4a^2c^2(s_{11}+s_{33}-2s_{13})+(a^2-c^2)^2s_{44}}{(a^2+c^2)^2}$	Zn, Cd, Co
	Cubic system	
$(001)\ [100]$	s_{44}	TlBr-TlI
$(001)\ ]110]$	s_{44}	Al
$(110)\ [001]$	s_{44}	NH_4Cl, NH_4Br, PbS, PbTe, AuZn, TlCl-TlBr, TlBr-TlI
$(110)\ [1\bar{1}0]$	$2(s_{11}-s_{12})$	NaCl, KCl, KBr, KI, LiF
$(1\bar{1}0)\ [111]$	$\frac{4}{3}(s_{11}-s_{12})+\frac{1}{3}s_{44}$	α-Fe, Mo, Nb, β-CuZn
$(111)\ [1\bar{1}0]$	$\frac{4}{3}(s_{11}-s_{12})+\frac{1}{3}s_{44}$	Ge, Ag, Au, Ni, Cu, CuAu, AlCu, AlZn, α-CuZn
$(11\bar{2})\ [111]$	$\frac{4}{3}(s_{11}-s_{12})+\frac{1}{3}s_{44}$	α-Fe
$(12\bar{3})\ [111]$	$\frac{4}{3}(s_{11}-s_{12})+\frac{1}{3}s_{44}$	α-Fe, AgMg

Notation: a, c are lattice parameters, γ^* is the angle between principal vectors of the reciprocal lattice.

is in equilibrium. Force σ is exerted on unit area. The ends are free of loads. In this case we have *shear* stresses in the rod; they are

$$\boldsymbol{\sigma} = \sigma(\boldsymbol{pq} + \boldsymbol{qp}), \quad \sigma_{ij} = \sigma(p_i q_j + q_i p_j) \tag{53.18}$$

($\boldsymbol{p}$ and $\boldsymbol{q}$ are unit vectors of the normals to side faces). Strains can be expressed as

$$\boldsymbol{\varepsilon} = 2\sigma \mathbf{s} : \boldsymbol{pq}, \quad \varepsilon_{ij} = 2\sigma s_{ijkl} p_k q_l \tag{53.19}$$

(use has been made of the symmetry of tensor $\boldsymbol{\varepsilon}$ with respect to the last two indices). Of particular interest is the shear component of the strain tensor $\boldsymbol{p} \cdot \boldsymbol{\varepsilon} \cdot \boldsymbol{q} = 2\sigma \boldsymbol{pq} : \mathbf{s} : \boldsymbol{pq} = 2\sigma s_{ijkl} p_i q_j p_k q_l$. For a pair of mutually perpendicular directions $\boldsymbol{p}$ and $\boldsymbol{q}$ the ratio of the force exerted on unit of surface area to the double shear component of the strain tensor is called *the shear modulus* $G(\boldsymbol{p}, \boldsymbol{q})$. The shear modulus is defined by the formula

$$G^{-1}(\boldsymbol{p}, \boldsymbol{q}) = 4\boldsymbol{pq} : \mathbf{s} : \boldsymbol{pq} = 4 s_{ijkl} p_i q_j p_k q_l. \tag{53.20}$$

More convenient for computations is the form

$$G^{-1}(\boldsymbol{p}, \boldsymbol{q}) = s_{\lambda\mu} (\boldsymbol{pq} + \boldsymbol{qp})_\lambda (\boldsymbol{pq} + \boldsymbol{qp})_\mu, \tag{53.21}$$

where

$$(\boldsymbol{pq} + \boldsymbol{qp})_\lambda = p_i q_j + q_i p_j \quad (ij \leftrightarrow \lambda = 1, \ldots, 6).$$

For the derivation of this formula see Appendix F.

Formulas (53.20) and (53.21) show that the shear modulus $G(\boldsymbol{p}, \boldsymbol{q})$ is symmetric with respect to directions $\boldsymbol{p}$ and $\boldsymbol{q}$:

$$G(\boldsymbol{p}, \boldsymbol{q}) = G(\boldsymbol{q}, \boldsymbol{p}). \tag{53.22}$$

It is fairly difficult to realize experimentally uniformly distributed tangential forces on a surface with any degree of accuracy, but the shear modulus defined by formula (53.22) plays an important role in the theory of dislocations. Indeed if $\boldsymbol{n}$ is the unit vector of the perpendicular to the glide plane, and $\boldsymbol{l}$ is the unit vector of the glide direction, then for the dislocations in the given glide system the most essential characteristic of the elastic properties of a crystal is exactly the shear modulus $G(\boldsymbol{n}, \boldsymbol{l})$.

If the glide elements—a plane and a direction—are specified by Miller indices $(n_1 n_2 n_3)$ and $[l^1 l^2 l^3]$, the reciprocal of the shear modulus can be computed with the aid of formula

$$G^{-1}(\boldsymbol{n}, \boldsymbol{l}) = \frac{s_{ijkm} E_i^\alpha E_k^\beta A_{\gamma j} A_{\delta m} n_\alpha n_\beta l^\gamma l^\delta}{g^{\varepsilon\xi} n_\varepsilon n_\xi q_{\eta\zeta} l^\eta l^\zeta}, \tag{53.23}$$

where E_i^α and $A_{\gamma j}$ are the elements of matrices relating the mutually perpendicular unit vectors of the crystal-physical system of coordinates to the base vectors of the crystal lattice (see Sec. 16 and Appendix B). The results of such computations for a series of crystals are given in Table 53.3.

As distinct from isotropic bodies, anisotropic ones experience volume expansion (or compression) under shear stresses. It is $\Delta V/V = \varepsilon_{ii} = 2\sigma s_{iikl}p_k q_l = 2\sigma S_{kl}p_k q_l$ where **S** is the tensor of the compressibility coefficients. Since vectors $\boldsymbol{p}$ and $\boldsymbol{q}$ are mutually perpendicular, $\delta_{kl}p_k q_l = 0$; hence the volume expansion under shear stressis is defined by the deviator of the uniform extension tensor

$$\frac{\Delta V}{V} = 2\sigma R_{kl}p_k q_l. \tag{53.24}$$

Sec. 54. Bending and Twisting of Crystals

In the preceding Section we discussed simple states of stress under which the stress tensor does not depend on the Cartesian coordinates; here we consider some simple states of stress which are characterized by the linear dependence of the tensor on the coordinates*.

Bending of a Rectangular Crystal Bar. Let us discuss a rectangular crystal bar, $2c$ long, $2a$ wide, $2b$ thick, to the ends of which there are

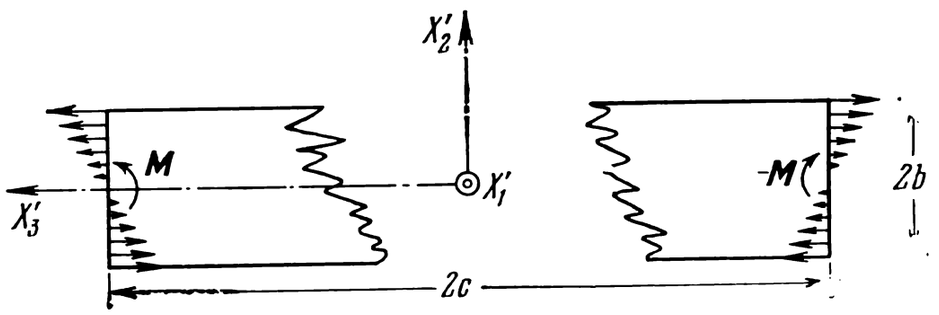


Fig. 54.1. Bend of a crystal bar: special coordinate system, bending forces and moments

applied bending moments $\boldsymbol{M}$ and $-\boldsymbol{M}$ respectively. Let us connect the bar with a special, generally speaking, non-crystal-physical system of Cartesian coordinates $OX_1'X_2'X_3'$ as shown in Fig. 54.1. We denote the mutually perpendicular unit vectors $\boldsymbol{e}_1'$, $\boldsymbol{e}_2'$, and $\boldsymbol{e}_3'$ by $\boldsymbol{m}$, $\boldsymbol{n}$ and $\boldsymbol{q}$ respectively. The bending moments $\boldsymbol{M}$ and $-\boldsymbol{M}$ can be created, for instance**, by a set of loads shown schematically in Fig. 54.1; to the end $x_3' = c$ forces $\boldsymbol{P} = kx_2'\boldsymbol{q}$ are applied (per unit area), and to the end $x_3' = -c$ are applied forces $\boldsymbol{P}$.

The bending moment of forces applied to the end $x_3' = c$ is

$$\boldsymbol{M} = \int_S x_2'\boldsymbol{n} \times \boldsymbol{P}\, dS = \int_{-a}^{a}\int_{-b}^{b} x_2'\boldsymbol{n} \times kx_2'\boldsymbol{q}\, dx_1'\, dx_2' = \frac{4}{3}ab^3k\boldsymbol{m}; \tag{54.1}$$

* See Rovenskaya, Sirotin and Voroshilov (1972); Sirotin and Rovenskaya (1973).

** *Saint-Venant's principle* is used here, see Leibenson (1947, Sec. 49).

hence we find $k = 3M/4ab^3$ and express the boundary conditions at the bar ends $x_3' = \pm c$ in terms of the twisting moment M. They are $\sigma\cdot(\pm q) = \pm (3M/4ab^3)\, x_2' q$. These boundary conditions (as well as the elastic equilibrium equations) are satisfied by the stress tensor

$$\sigma = \frac{3M}{4ab^3} x_2' qq; \tag{54.2}$$

only one its component $\sigma_3' = (3M/4ab^3)\, x_2'$ is non-zero in the special coordinate system. According to Hooke's law, the components of the strain tensor are

$$\varepsilon_\lambda' = \frac{3M}{4ab^3} s_{\lambda 3}' x_2'. \tag{54.3}$$

The primes here, as in the preceding formulas, show that the given tensor quantity is referred not to a crystallographic but to a special system of coordinates*. Thus the coefficients s_{λ_3}' do not coincide at all with the values of the elastic compliance coefficients given in the Tables, provided that the edges of the bar are not directed along the corresponding axes of the crystal-physical system of coordinates; they are referred to the Table values of the elastic compliance coefficients of a given crystal $s_{\mu\nu}$ by relations $s_{\lambda 3}' = P_{\lambda'\mu} p_{3'\nu} s_{\mu\nu}$ in which the elements of the transformation matrix $P_{\lambda'\nu}$ are defined by the cosines of the angles between the axes of the special and crystal-physical coordinate systems $c_{i'j} = \cos(X_i' X_j)$, see Appendix F.

The bend of the bar is characterized by a gradual change of the component φ_1' of the vector of small rotations in the progress along the bar, i.e. in the direction of the X_3' axis: bend $\psi = \partial\varphi_1'/\partial x_3'$. According to (49.17), $\partial\varphi_1'/\partial x_3' = \operatorname{curl} \varepsilon_{13}'$. Having calculated the right-hand side of this equality with the aid of formula (43.13), we find

$$\psi = \frac{\partial \varepsilon_{33}'}{\partial x_2'} - \frac{\partial \varepsilon_{23}'}{\partial x_3'} = \frac{\partial \varepsilon_3'}{\partial x_2'} - \frac{1}{2}\frac{\partial \varepsilon_4'}{\partial x_3'}. \tag{54.4}$$

Substituting here expressions (54.3) for the components of the strain tensor, we obtain

$$\psi = \frac{3 s_{33}'}{4ab^3} M. \tag{54.5}$$

The ratio $D = M/\psi$ is usually called the *bending stiffness* of the bar. Noting that $1/s_{33}'$ is Young's modulus $E(q)$ in the direction of the bar length we have

$$D(q) = \frac{4}{3} ab^3 E(q). \tag{54.6}$$

* Strictly speaking, the primes should be placed over the indices as was done earlier; they are placed over the quantities themselves just for simplicity.

We find that the bending stiffness is independent (if the direction of vector $\boldsymbol{q}$ is specified) of the orientation of vectors $\boldsymbol{m}$ and $\boldsymbol{n}$.

In distinction from isotropic bodies, anisotropic ones experience twisting in bending. The twisting of the bar is naturally characterized by the change of the component φ_3' of the axial vector of small rotations along the rod axis X_3', i.e. by the derivative $\vartheta = \partial\varphi_3'/\partial x_3'$. Again, using formulas (49.17) and (43.13), we obtain

$$\vartheta = \frac{\partial\varepsilon_{23}'}{\partial x_1'} - \frac{\partial\varepsilon_{13}'}{\partial x_2'} = \frac{1}{2}\left(\frac{\partial\varepsilon_4'}{\partial x_1'} - \frac{\partial\varepsilon_5'}{\partial x_2'}\right), \tag{54.7}$$

and substituting here expression (54.3) for the strain tensor components, we find

$$\vartheta = -\frac{3s_{35}'}{8ab^3}M. \tag{54.8}$$

Noting that $s_{35}' = 2s_{3331}' = 2\boldsymbol{qq} : \mathbf{s} : \boldsymbol{qm}$, we refer the twisting to an arbitrary system of coordinates:

$$\vartheta = -\frac{3M}{4ab^3}s_{ijkl}q_iq_jq_km_l. \tag{54.9}$$

This formula is also valid for the crystal-physical system of coordinates. For convenient use of tabulated values of the elastic compliance coefficients $s_{\lambda\mu}$ in calculations it is expedient to transform (54.9) into

$$\vartheta = -\frac{3M}{8ab^3}s_{\lambda\mu}(\boldsymbol{qq})_\lambda(\boldsymbol{qm}+\boldsymbol{mq})_\mu; \tag{54.10}$$

$$(\boldsymbol{qq})_\lambda = q_iq_j \quad (ij \leftrightarrow \lambda = 1, \ldots, 6),$$

$$(\boldsymbol{qm}+\boldsymbol{mq})_\mu = q_km_l + m_kq_l$$

$$(kl \leftrightarrow \mu = 1, \ldots, 6).$$

The bar volume does not change in bending: the expansion of one its half is compensated by the compression of the other.

Twisting of a Round Crystal Rod. Let us consider an anisotropic round rod of radius R and length $2l$ to the ends of which torques $\boldsymbol{K}$ and $-\boldsymbol{K}$ are applied, while the lateral surface is free of loads. We introduce a special Cartesian system of coordinates generally differing from the crystal-physical one, with the origin at the centre of the rod; the axis X_3' of the system (with unit vector $\boldsymbol{e}_3' = \boldsymbol{q}$) coincides with the rod axis, while axes X_1' and X_2' (with unit vector $\boldsymbol{e}_1' = \boldsymbol{m}$ and $\boldsymbol{e}_2' = \boldsymbol{n}$) are perpendicular to it and to each other, being arbitrary for the rest. Moreover, we introduce at each point a local system of coordinates constructed on mutually orthogonal unit vectors $\boldsymbol{e}_r$, $\boldsymbol{e}_\varphi$ and $\boldsymbol{q}$ directed along the coordinate lines of a cylindrical system of coordinates (Fig. 54.2). The cylindrical system of coordinates is referred to the special one by the relations $x_1' = r\cos\varphi$, $x_2' = r\sin\varphi$.

The torque $\boldsymbol{K}$ can be developed, in particular, by forces $\boldsymbol{P} = kr\boldsymbol{e}_\varphi$ applied to the end $x_3' = l$ per unit area. Then

$$\boldsymbol{K} = \int_S \boldsymbol{r} \times \boldsymbol{P}\, dS = \int_0^{2\pi} \int_0^R r\boldsymbol{e}_r \times kr\boldsymbol{e}_\varphi r\, dr\, d\varphi = \frac{1}{2}\pi R^4 k\boldsymbol{q}, \quad (54.11)$$

whence we find $k = 2K/\pi R^4$. Boundary conditions $\boldsymbol{\sigma}\cdot\boldsymbol{q} = (2K/\pi R^4)\, r\boldsymbol{e}_\varphi$, $\boldsymbol{\sigma}\cdot\boldsymbol{e}_r = 0$ are satisfied by the stress tensor

$$\boldsymbol{\sigma} = \frac{2K}{\pi R^4}\, r\,(\boldsymbol{e}_\varphi\boldsymbol{q} + \boldsymbol{q}\boldsymbol{e}_\varphi). \quad (54.12)$$

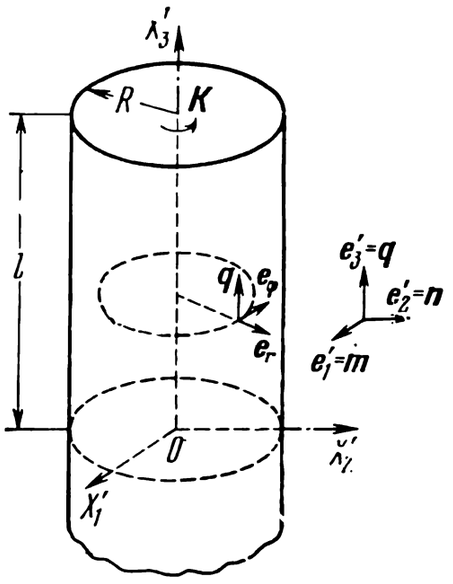


Fig. 54.2. Special and local coordinate systems for the solution of a problem on the torsion of a round rod

To express it in the special system of coordinates we should note that $r\boldsymbol{e}_\varphi = x_1'\boldsymbol{n} - x_2'\boldsymbol{m}$. Thus

$$\boldsymbol{\sigma} = \frac{2K}{\pi R^4}\,[x_1'\,(\boldsymbol{nq} + \boldsymbol{qn}) - x_2'\,(\boldsymbol{mq} + \boldsymbol{qm})]. \quad (54.13)$$

For the calculation of strains we write down the stress tensor components

$$\sigma_\mu' = \frac{2K}{\pi R^4}\,(x_1'\delta_{4\mu} - x_2'\delta_{5\mu}); \quad (54.14)$$

This notation directly follows from (54.13). Strains ε_λ' are

$$\varepsilon_\lambda' = \frac{2K}{\pi R^4}\,(s_{\lambda 4}'x_1' - s_{\lambda 5}'x_2'). \quad (54.15)$$

Axial torsion per unit of the rod length is $\vartheta = \partial\varphi_3'/\partial x_3'$. Using formulas (49.17) and (43.13) again, we find

$$\vartheta = \frac{\partial\varepsilon_{23}'}{\partial x_1'} - \frac{\partial\varepsilon_{13}'}{\partial x_2'} = \frac{1}{2}\left(\frac{\partial\varepsilon_4'}{\partial x_1'} - \frac{\partial\varepsilon_5'}{\partial x_2'}\right). \quad (54.16)$$

Taking (54.15) into account, we obtain

$$\vartheta = \frac{K}{\pi R^4}\,(s_{44}' + s_{55}'). \quad (54.17)$$

The ratio $C = K/\vartheta$ is called *the torsion stiffness* of the rod; evidently

$$C = \frac{\pi R^4}{(s_{44}' + s_{55}')}. \quad (54.18)$$

To express stiffness C in terms of tabulated values of the elastic compliance coefficients, we shall consider the expression

$$\frac{1}{4}\,(s_{44}' + s_{55}') = s_{2323}' + s_{1313}' = s_{2323}' + s_{1313}' + s_{3333}' - s_{3333}' = s_{k3k3}' - s_{3333}'.$$

Here the elastic compliance coefficients are still referred to the special system of coordinates, but they can be now expressed in terms of a single unit vector $\boldsymbol{q}$ directed along the X_3' coordinate axis. Since in the arbitrary Cartesian system of coordinates this expression can be written in the form

$$s_{kjkl}q_jq_l - s_{ijkl}q_iq_jq_kq_l = s_{ijkl}(\delta_{ik} - q_iq_k)\,q_jq_l,$$

where q_j are the components of the unit vector $\boldsymbol{q}$ with respect to this system, the torsion stiffness of the rod will be

$$C(\boldsymbol{q}) = \frac{\pi R^4}{4s_{ijkl}(\delta_{ik} - q_iq_k)\,q_jq_l}. \tag{54.19}$$

In an isotropic body $s_{44} = s_{55} = 1/G$ (G is the shear modulus), so that its torsion stiffness $C = \pi R^4 G/2$. Therefore quantity

$$G(\boldsymbol{q}) = \frac{2C(q)}{\pi R^4}\,\frac{1}{2s_{ijkl}(\delta_{ik} - q_iq_k)\,q_jq_l} \tag{54.20}$$

is called *the shear modulus of anisotropic material for torsion.* With the aid of a symmetric second-rank matter tensor $Z_{jl} = s_{kjkl}$ and formulas (53.9) it is possible to express the reciprocal of the shear modulus $G^{-1}(\boldsymbol{q})$ in a form convenient for calculations

$$G^{-1}(\boldsymbol{q}) = 2(\boldsymbol{q}\cdot\boldsymbol{Z}\cdot\boldsymbol{q} - E^{-1}(\boldsymbol{q})), \tag{54.21}$$

where $E^{-1}(\boldsymbol{q})$ is Young's modulus reciprocal. The form of tensor Z for all classes of elastic symmetry is given in Table 54.1.

Since anisotropic rods experience twisting in bending, it can be expected that they will bend when subjected to twisting. As a matter of fact, having calculated

$$\psi_1' = \frac{\partial\varphi_1'}{\partial x_3'} = \frac{\partial\varepsilon_{33}'}{\partial x_2'} - \frac{\partial\varepsilon_{23}'}{\partial x_3'} = \frac{2K}{\pi R^4}\,s_{35}',$$

$$\psi_2' = \frac{\partial\varphi_2'}{\partial x_3'} = \frac{\partial\varepsilon_{13}'}{\partial x_3'} - \frac{\partial\varepsilon_{33}'}{\partial x_1'} = -\frac{2K}{\pi R^4}\,s_{34}',$$

we find that the axis of bend is parallel to vector $s_{35}'\boldsymbol{m} + s_{34}'\boldsymbol{n}$ while its magnitude is

$$\psi = \frac{2K}{\pi R^4}\sqrt{(s_{35}')^2 + (s_{34}')^2}.$$

Again this expression depends only on the crystallographic orientation of the rod axis, i.e. on the components q_i of its unit vector $\boldsymbol{q}$. In an arbitrary, in particular in the crystal-physical system of coordinates,

$$\psi = \frac{4K}{\pi R^4}\sqrt{\boldsymbol{qqq}\,\vdots\,\mathbf{s}\cdot(\mathbf{I} - \boldsymbol{qq})\cdot\mathbf{s}\,\vdots\,\boldsymbol{qqq}}\,.$$

The representation surfaces of Young's modulus of the extension coefficients $E^{-1}(\boldsymbol{q})$, torsion coefficients $G^{-1}(\boldsymbol{q})$, and Poisson $\nu(\boldsymbol{q})$

Table 54.1

Tensor $Z_{ij}=s_{ikjk}$ for all the Crystallographic and Limit Classes (see formula (54.21))

Systems	$Z_{ij}=s_{ikjk}$		
Triclinic	$s_{11}+1/4s_{55}+1/4s_{66}$ $1/4s_{45}+1/2s_{16}+1/2s_{26}$ $1/4s_{64}+1/2s_{35}+1/2s_{15}$	$1/4s_{45}+1/2s_{16}+1/2s_{26}$ $s_{22}+1/4s_{66}+1/4s_{44}$ $1/4s_{56}+1/2s_{24}+1/2s_{34}$	$1/4s_{64}+1/2s_{35}+1/2s_{15}$ $1/4s_{56}+1/2s_{24}+1/2s_{34}$ $s_{33}+1/4s_{44}+1/4s_{55}$
Monoclinic $2\|X_2$	$s_{11}+1/4s_{55}+1/4s_{66}$ 0 $1/4s_{64}+1/2s_{35}+1/2s_{15}$	0 $s_{22}+1/4s_{66}+1/4s_{44}$ 0	$1/4s_{64}+1/2s_{35}+1/2s_{15}$ 0 $s_{33}+1/4s_{44}+1/4s_{55}$
$2\|X_3$	$s_{11}+1/4s_{55}+1/4s_{66}$ $1/4s_{45}+1/2s_{16}+1/2s_{26}$ 0	$1/4s_{45}+1/2s_{16}+1/2s_{26}$ $s_{22}+1/4s_{66}+1/4s_{44}$ 0	0 0 $s_{33}+1/4s_{44}+1/4s_{55}$
Rhombic	$s_{11}+1/4s_{55}+1/4s_{66}$ 0 0	0 $s_{22}+1/4s_{66}+1/4s_{44}$ 0	0 0 $s_{33}+1/4s_{44}+1/4s_{55}$
Tetragonal	$s_{11}+1/4s_{44}+1/4s_{66}$ 0 0	0 $s_{11}+1/4s_{44}+1/4s_{66}$ 0	0 0 $s_{33}+1/2s_{44}$
Trigonal and hexagonal systems and textures	$3/2s_{11}-1/2s_{12}+1/4s_{44}$ 0 0	0 $3/2s_{11}-1/2s_{12}+1/4s_{44}$ 0	0 0 $s_{33}+1/2s_{44}$
Cubic	$s_{11}+1/2s_{44}$ 0 0	0 $s_{11}+1/2s_{44}$ 0	0 0 $s_{11}+1/2s_{44}$
Isotropic bodies	$2s_{11}-s_{12}$ 0 0	0 $2s_{11}-s_{12}$ 0	0 0 $2s_{11}-s_{12}$

ratios for a number of crystals are shown in some figures in Sec. 24 and in Figs. 54.3-54.10. For crystals of the cubic system they are shown in Figs. 24.4*a* and *b* and 24.7. If the elastic compliance tensor

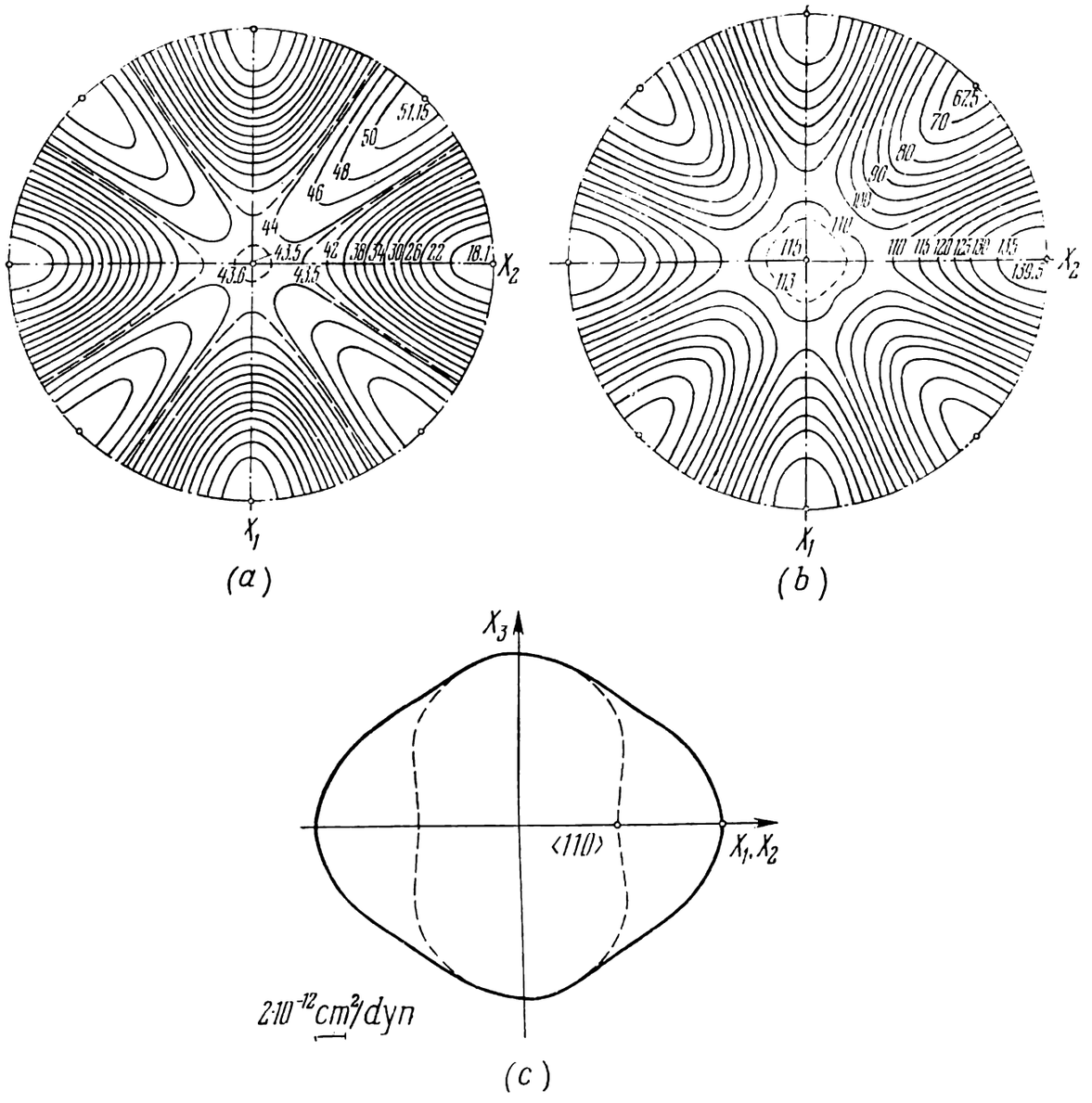


Fig. 54.3. Representation surfaces of the elastic properties of a crystal of ammonium dihydrophosphate (ADP), class $\bar{4}2m$: (a) $E^{-1}(q)$, stereogram; (b) $G^{-1}(q)$, stereogram; in 10^{-13} cm²/dyn; (c) $G^{-1}(q)$, sections. Surface symmetry $4/mmm$

s for the crystals of the cubic system is written down in the form of (52.13), then the equations of the representation surfaces $E^{-1}(q)$ and $G^{-1}(q)$ become

$$r = E^{-1}(q) = S_I^{\{4\}} + S_N N^0_{ijkl} q_i q_j q_k q_l, \tag{54.22}$$

$$r = G^{-1}(q) = \frac{4}{3}\left(S_I^{\{4\}} - S_I^{\{22\}}\right) - 2S_N^{\{4\}} N^0_{ijkl} q_i q_j q_k q_l, \tag{54.23}$$

where the coefficients S_I are defined by formulas (52.15), and the nonor $\mathbf{N}^0$ by formula (52.14). Thus the radius-vectors of the repre-

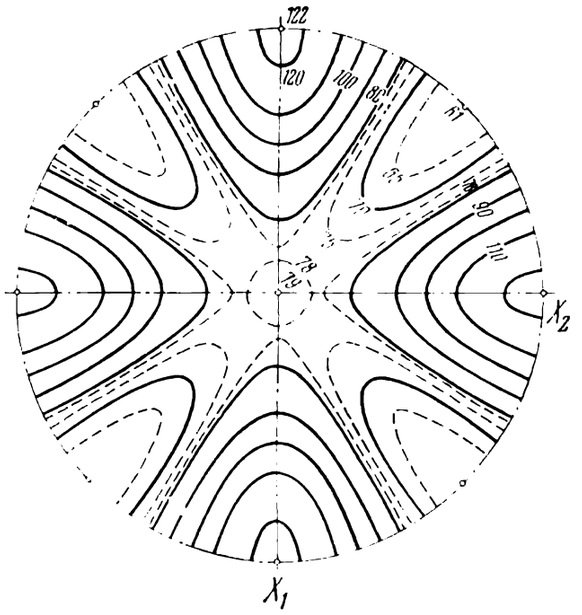


Fig. 54.4. Stereogram of the representation surface of the twisting coefficient G^{-1} (q) of a crystal of potassium dihydrophospate (KDP), class $\bar{4}2m$. Surface symmetry $4/mmm$; in 10^{-13} cm²/dyn

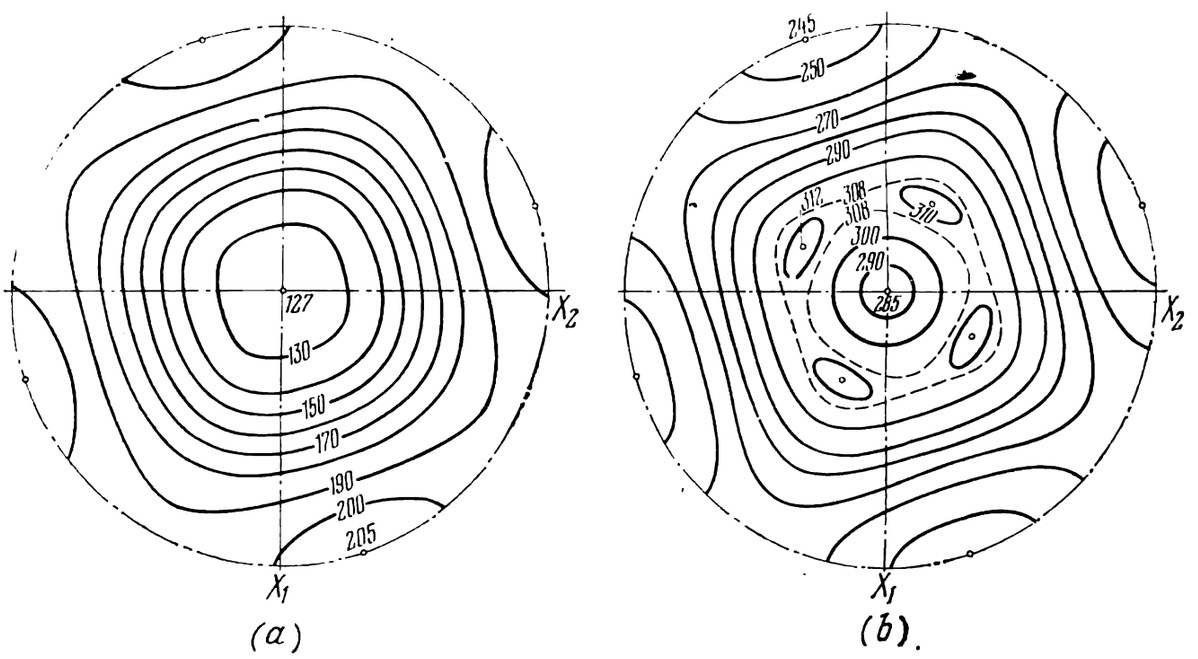


Fig. 54.5. Stereograms of the representation surfaces: (a) of the tension coefficient E^{-1} (q); (b) of the twisting coefficient G^{-1} (q) of a crystal of pentaerythrite, class 4, Laue class $4/m$. Symmetry of surfaces is $4/mmm$; in 10^{-13} cm²/dyn

sentation surfaces consist of a constant term (in 54.22) it is $S_I^{\{4\}}$) and of the normal component of the nonor $\mathbf{N}^0$ $[m3m]$ multiplied by a certain coefficient (in (54.22) it is $S_N^{\{4\}}$). It can be said that the representation surfaces (54.22) and (54.23) are linear combinations of the representation surfaces of a unit scalar (of sphere $r = 1$) and of a unit nonor $\mathbf{N}^0$ $[m3m]$ (see Fig. 47.5). Thus the representation

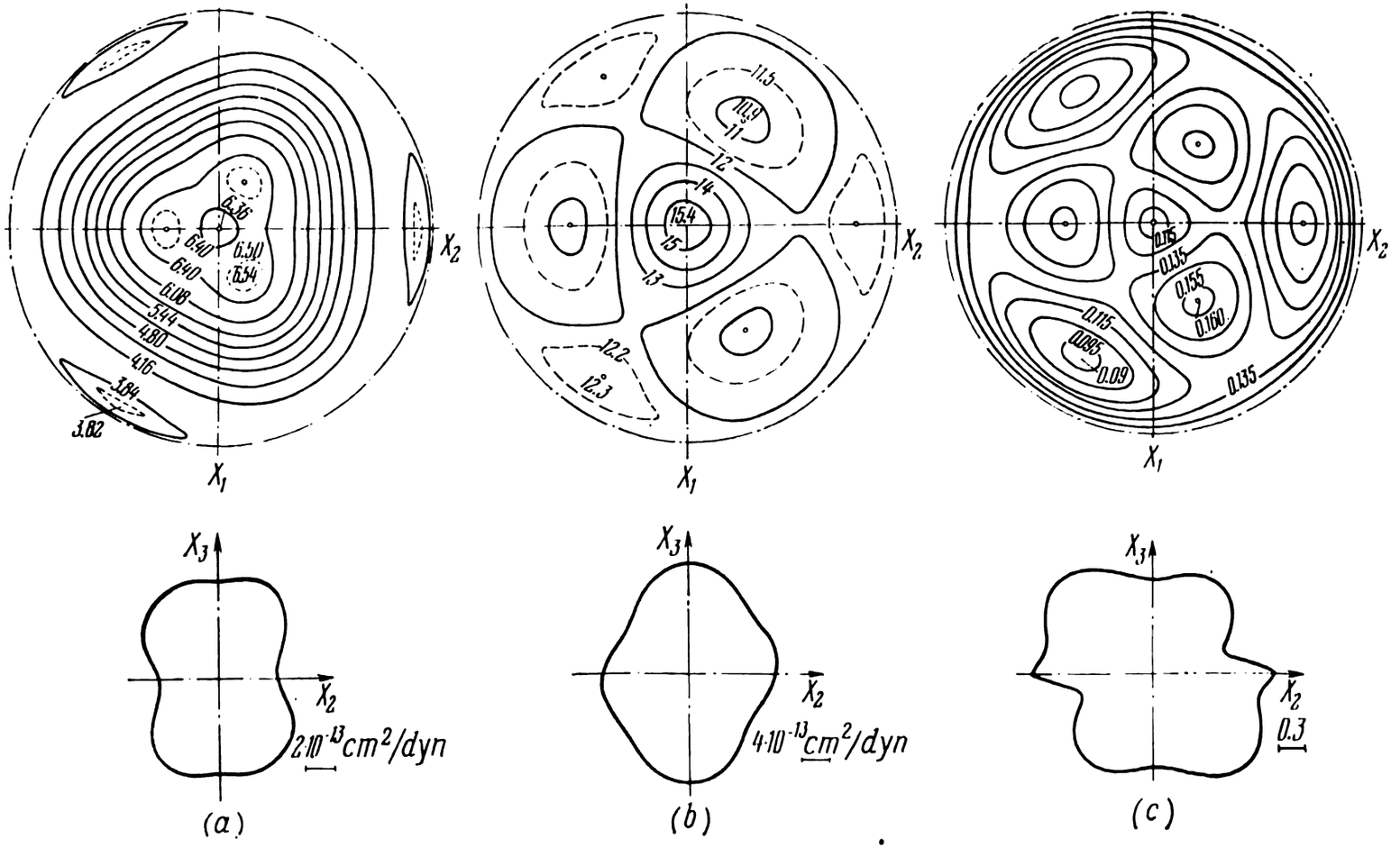


Fig. 54.6. Stereograms (upper row) and sections by the plane X_2X_3 (lower row) of representation surfaces of the elastic properties of a tourmaline crystal, class $3m$: (a) of the tension coefficient $E^{-1}(q)$; in 10^{-13} cm²/dyn, (b) of the coefficient $G^{-1}(q)$; in 10^{-13} cm²/dyn, (c) of Poisson's ratio $\nu(q)$. Symmetry of surfaces is $\bar{3}m$. The plane X_1X_2 is isotropic

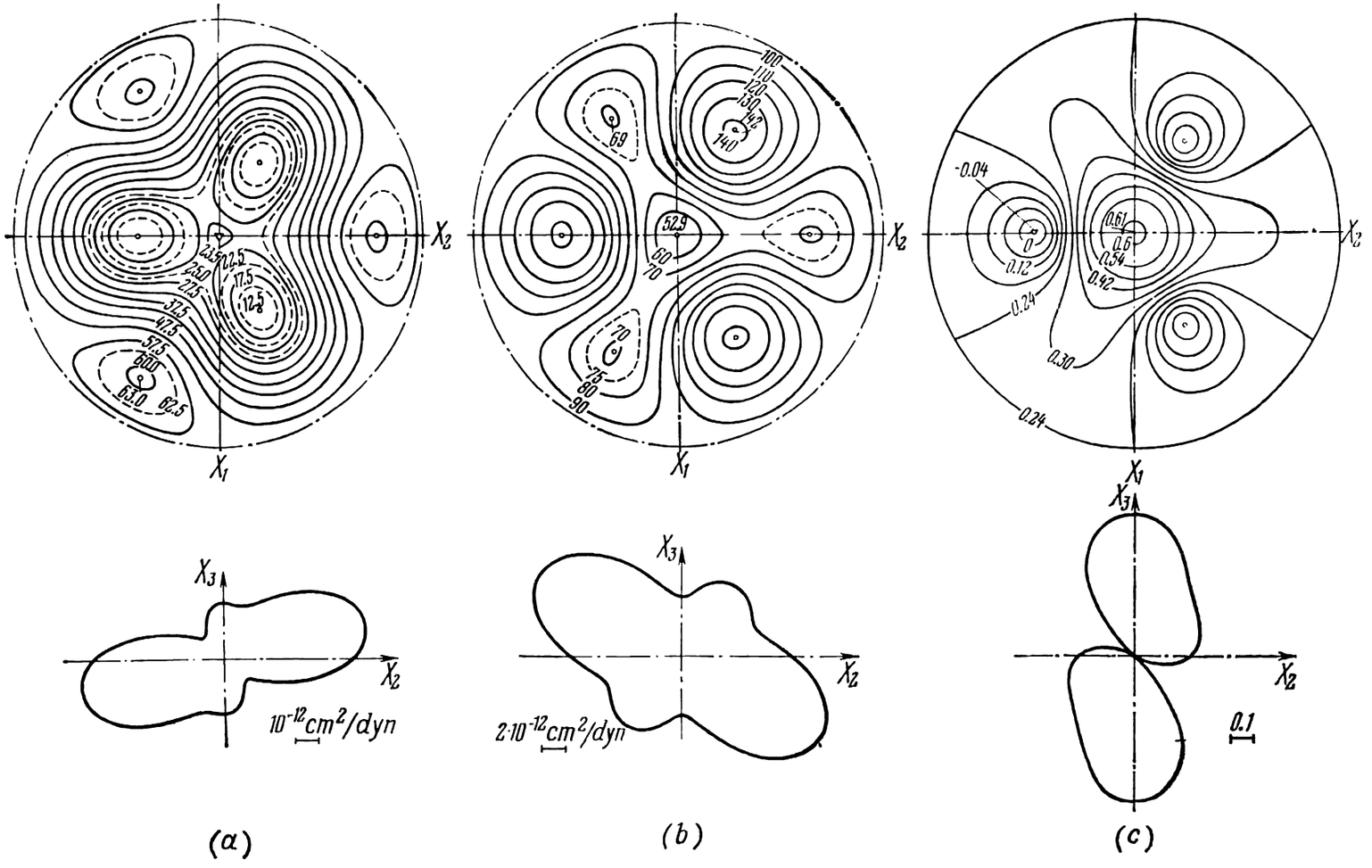


Fig. 54.7. Stereograms (upper row) and sections by the plane X_2X_3 (lower row) of the representation surfaces of the elastic properties of a tellurium crystal, class 32:
(a) of the tension coefficient $E^{-1}(q)$; in 10^{-13} cm²/dyn; (b) of the twisting coefficient $G^{-1}(q)$; in 10^{-13} cm²/dyn; (c) of Poisson's ratio $\nu(q)$. Symmetry of surfaces is $\bar{3}m$. The plane X_1X_2 is isotropic

surface shown in Fig. 47.5 is universal representation surface for anisotropy of the elastic properties of all cubic crystals. It shows, in particular that planes {111} are isotropic for them and directions ⟨100⟩ and ⟨111⟩ are the extreme ones.

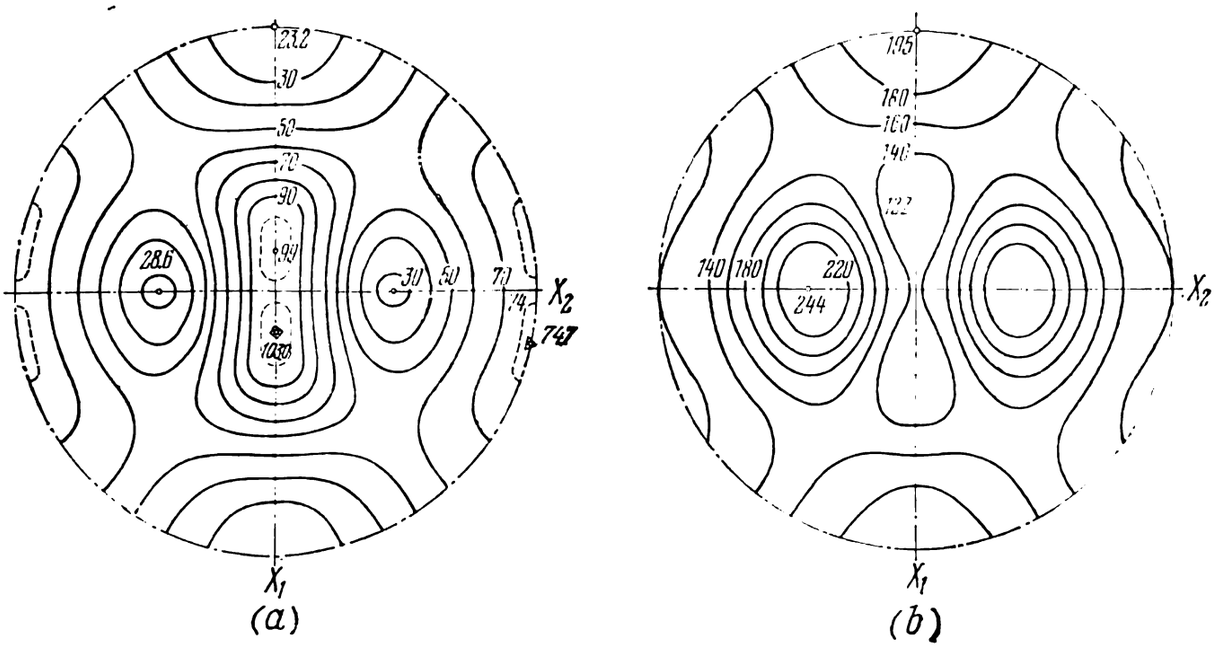


Fig. 54.8. Stereograms of the representation surfaces: (a) of the tension coefficient $E^{-1}(q)$; (b) of the twisting coefficient $G^{-1}(q)$ of $KB_5O_8 \cdot 4H_2O$ crystal-class $mm2$. Symmetry of surfaces is mmm; in 10^{-13} cm²/dyn

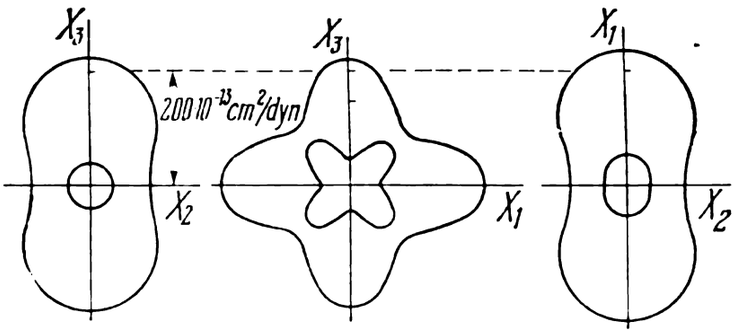


Fig. 54.9. Sections by the coordinate planes of the representation surfaces of the tension coefficient $E^{-1}(q)$ (internal surface) and of the coefficient $G^{-1}(q)$ (external surface) of a Rochelle salt crystal, class 222. Symmetry of surfaces is mmm (Wooster, 1949)

The representation surfaces $E^{-1}(q)$ and $G^{-1}(q)$ for crystals which are transversally isotropic by their elastic properties are shown in Fig. 24.6. If tensor s is written in the form of (52.9), their equations will be

$$r = E^{-1}(q) = S_I^{\{4\}} + S_D^{\{4\}} D_{ij}^0 q_i q_j + S_N^{\{4\}} N_{ijkl}^0 q_i q_j q_k q_l, \tag{54.24}$$

$$r = G^{-1}(q) = \frac{4}{3}(S_I^{\{4\}} - S_I^{\{22\}}) + \frac{1}{3}(S_D^{\{4\}} - S_D^{\{22\}}) D_{ij}^0 q_i q_j - \\ - 2S_N^{\{4\}} N_{ijkl}^0 q_i q_j q_k q_l \tag{54.25}$$

where $\mathbf{D}^0$ and $\mathbf{N}^0$ are defined by formulas (52.10) and (52.11) respectively. Thus these surfaces are linear combinations of the sphere and representation surfaces of tensors $\mathbf{D}^0$ $[\infty/mm]$ and $\mathbf{N}^0$ $[\infty/mm]$ (see Figs. 47.1*b* and *d*). The expansion coefficients characterize the role of individual irreducible tensors in the formation of the representation surface.

Figs. 54.3-54.5 show the stereographic projections and sections of the representation surfaces of the elastic properties of the tetragonal system crystals. These surfaces can be represented as linear combinations of the sphere and representation surfaces $\mathbf{D}^0$ $[\infty/mm]$, $\mathbf{N}^0$ $[\infty/mm]$ and $\mathbf{N}^0$ $[m3m]$. Fig. 54.5 shows that the crystals of Laue class $4/m$ also have the $4/mmm$ symmetry of elastic properties, but their symmetry planes of elastic properties are not related to the crystal-physical coordinate axes.

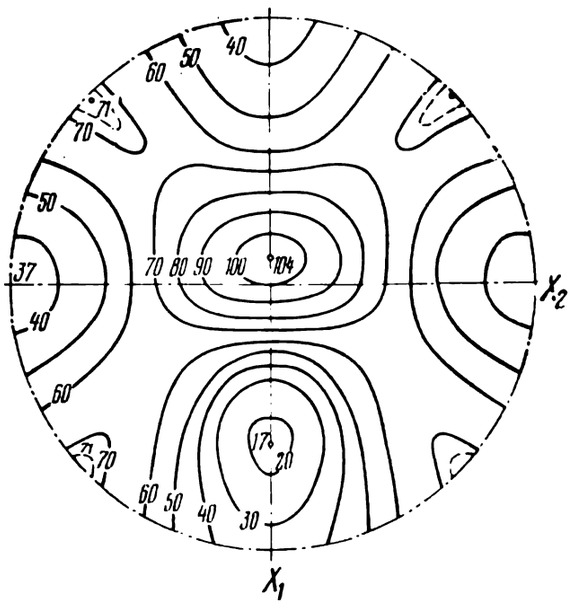


Fig. 54.10. Representation surface of the extension coefficient E^{-1} (q) of a crystal of ethylene diamine tartrate (EDT), class 2. (Stereogram). Symmetry of surface is $2/m$; in 10^{-13} cm²/dyn

The representation surfaces $E^{-1}(\boldsymbol{q})$ and $G^{-1}(\boldsymbol{q})$ of the trigonal system crystals (see also Figs. 24.8-24.11, 54.6 and 54.7) are also linear combinations of the sphere and surfaces $\mathbf{D}^0$ $[\infty/mm]$, $\mathbf{N}^0$ $[\infty/mm]$ and $\mathbf{N}^0$ $(m3m]$, but the latter is taken in the "rhombohedral" orientation (see Fig. 47.5*b*). Since for all the components the X_1X_2 plane, i.e. (0001), is isotropic, it is also isotropic for the elastic properties, which is corroborated by all the figures here shown. It can be seen in Fig. 54.7*c* that Poisson's ratio ν (**q**) in crystals can have not only negative values but also values exceeding 0.5, which is impossible in isotropic bodies (see formula (63.23)).

The surfaces of elastic properties of the rhombic system crystals, shown in Figs. 24.5, 54.8 and 54.9 can be obtained by linear combinations from a set of surfaces for the tetragonal crystals supplemented by Fig. 47.6. Finally, Fig. 54.10 shows surface E^{-1} $(\boldsymbol{q})$ for a monoclinic system crystal.

The equations of the representation surfaces of the elastic properties, in particular, (54.22)-(54.25) can be obtained as linear combinations of the equations of the surfaces of unit irreducible tensors given in Table 47.4.

Sec. 55. Temperature Stresses in Crystals

The equations of elastic equilibrium Div $\boldsymbol{\sigma} = 0$ and of compatibility of strains Inc $\boldsymbol{\varepsilon} = 0$ hold whether the whole crystal has the same temperature or the latter changes from one point of the crystal to another. In the latter case it is necessary, however, to take into account the temperature terms in Hooke's law

$$\varepsilon_\lambda = s_{\lambda\mu} + \alpha_\lambda \Theta, \qquad \boldsymbol{\varepsilon} = \mathbf{s} : \boldsymbol{\sigma} + \boldsymbol{\alpha}\Theta. \tag{55.1}$$

As a result the Beltrami-Michell equation becomes non-homogeneous: instead of (51.17) we have

$$\operatorname{Inc}(\mathbf{s} : \boldsymbol{\sigma}) = \operatorname{Inc}(\boldsymbol{\alpha}\Theta). \tag{55.2}$$

In uniform temperature fields all homogeneous bodies, isotropic or not, expand quite freely unless they are restricted by surrounding bodies. In non-uniform temperature fields, however, some parts of the body prevent the free expansion of its other parts, this resulting in the development of temperature stresses in a homogeneous body whose surface is free of any loads. The theorem of the unique solution of the theory of elasticity equations shows that the development of temperature stresses requires that the Beltrami-Michell equation (55.2) be non-homogeneous. This is satisfied only a at Inc $(\boldsymbol{\alpha}\Theta) \neq 0$, hence, the temperature stresses do not develop either in uniform temperature fields or in fields linearly dependent on the Cartesian coordinates.

On the other hand, condition Inc $(\boldsymbol{\alpha}\Theta) \neq 0$ is not only necessary but also sufficient for the development of temperature stresses. Indeed, if they are absent, the stress tensor $\boldsymbol{\varepsilon} = \boldsymbol{\alpha}\Theta$ must satisfy the compatibility equation Inc $\boldsymbol{\varepsilon} = 0$.

Since the crystal surface is free of loads, the average tensor of temperature stresses and the average moment of this tensor are zero, facts which follow directly from formulas (50.15) and (50.16). This fact is often used in the solution of problems on the distribution of thermoelastic stresses.

Let us discuss the simplest of such problems—the problem of thermoelastic stresses in a crystal plate $2a$ thick whose temperature varies only with thickness (Indenbom, Sylvestrova, Sirotin, 1956; Beloborodova, Rovenskaya, Sirotin, 1972).

Let us introduce a Cartesian system of coordinates $OX_1'X_2'X_3'$ with the origin in the middle plane of the plate. Let the axes X_1' and X_2', perpendicular to each other, be in the middle plane of the plate, and axis X_3' be directed along the perpendicular to it. Obviously not only temperature but also the stresses and strains depend neither on x_1' nor on x_2'.

Therefore the elastic equilibrium equations are

$$\frac{d\sigma'_{i3}}{dx'_3}=0 \tag{55.3}$$

(the prime shows that the components of tensor σ are referred to system $X'_1X'_2X'_3$). Their solutions σ'_{i3} are constants. They are all zero, since, according to (50.15),

$$\langle\sigma'_{i3}\rangle=\frac{1}{2a}\int\limits_{-a}^{a}\sigma'_{i3}\,dx'_3=0.$$

Thus

$$\sigma'_3=\sigma'_4=\sigma'_5=0, \tag{55.4}$$

and only three components, σ'_1, σ'_2 and σ'_6 differ from zero.

It follows from the compatibility equations, as was shown in Sec. 49 (formulas 49.20), that

$$\varepsilon'_\lambda=A'_\lambda+x'_3B'_\lambda \quad (\lambda=1,\ 2,\ 6), \tag{55.5}$$

where A'_λ and B'_λ are numbers independent of x'_3.

Taking (55.4) into account, Hooke's law (55.1) can be written

$$A'_\lambda+x'_3B'_\lambda=s'_{\lambda\mu}\sigma'_\mu+\alpha'_\lambda\Theta \quad (\lambda,\ \mu=1,\ 2,\ 6) \tag{55.6}$$

(the other three equalities of the generalized Hooke's law are of no importance to us).

Let us average equality (55.6) over the plate, i.e. integrate both its parts with respect to x'_3, from $-a$ to a, and divide the result by $2a$. Considering that the averaged stress tensor is zero, we have

$$A'_\lambda=\alpha'_\lambda\langle\Theta\rangle \quad (\lambda=1,\ 2,\ 6). \tag{55.7}$$

(The French quotes mean averaging over the plate.) Let us now multiply both sides of equality (55.6) by x'_3 and again average the result over the plate. Making use of the fact that the averaged moment of the stress tensor is also zero, we obtain

$$B'_\lambda=\frac{3}{a^2}\alpha'_\lambda\langle x'_3\Theta\rangle \quad (\lambda=1,\ 2,\ 6). \tag{55.8}$$

Thus, we have found three components of the strain tensor:

$$\varepsilon'_\lambda=\alpha'_\lambda\left(\langle\Theta\rangle+\frac{3}{a^2}x'_3\langle x'_3\Theta\rangle\right) \quad (\lambda=1,\ 2,\ 6). \tag{55.9}$$

Three equalities (55.6) rewritten as

$$S'_{\lambda\mu}\sigma'_\mu=\alpha'_\lambda\left(\langle\Theta\rangle+\frac{3}{a^2}x'_3\langle x'_3\Theta\rangle-\Theta\right) \quad (\lambda,\ \mu=1,\ 2,\ 6) \tag{55.10}$$

can be regarded as a system of three linear equations in three unknown components of the stress tensor, σ'_1, σ'_2, σ'_6. This system can be

easily solved by finding matrix $d'_{\varkappa\lambda}$, the reciprocal of matrix $s'_{\lambda\mu}$:

$$d'_{\varkappa\lambda}s'_{\lambda\mu} - \delta_{\varkappa\mu} \quad (\varkappa, \lambda, \mu = 1, 2, 6). \tag{55.11}$$

The field of thermoelastic stresses is defined by formulas

$$\sigma'_\varkappa = \begin{cases} d'_{\varkappa\lambda}\alpha'_\lambda \left(\langle\Theta\rangle + \frac{3}{a^2} x'_3 \langle x'_3\Theta\rangle - \Theta \right) & (\varkappa, \lambda = 1, 2, 6), \\ 0 & (\varkappa = 3, 4, 5). \end{cases} \tag{55.12}$$

Hence, with the aid of Hooke's law (55.1) we can also obtain the three still unknown components of the strain tensor.

If the temperature field is symmetric with respect to the middle plane of the plate: $\Theta(-x'_3) = \Theta(x'_3)$, then its average moment $\langle x'_3\Theta\rangle$ vanishes, and we have instead of (55.12)

$$\sigma'_\varkappa = \begin{cases} d'_{\varkappa\lambda}\alpha'_\lambda (\langle\Theta\rangle - \Theta) & (\varkappa, \lambda = 1, 2, 6), \\ 0 & (\varkappa = 3, 4, 5). \end{cases} \tag{55.13}$$

A temperature field symmetric with respect to the middle plane of the plate can be obtained, in particular, by uniform heating of the plate (see Sec. 33). In the notation of that paragraph formula (33.12) derived there becomes

$$\Theta - \langle\Theta\rangle = \frac{ha^2}{6k'_3}\left[3\left(\frac{x'_3}{a}\right)^2 - 1\right], \tag{55.14}$$

where h is the rate of temperature rise, $k'_3 = k'_{33}$ are the components of the temperature diffusivity tensor in system X'_1, X'_2, X'_3, a is the half-thickness of the plate. Thus under uniform heating of the crystal plate there develop thermoelastic stresses in it

$$\sigma'_\varkappa = \begin{cases} \frac{d'_{\varkappa\lambda}\alpha'_\lambda ha^2}{6k'_3}\left[1 - 3\left(\frac{x'_3}{a}\right)^2\right] & (\varkappa, \lambda = 1, 2, 6), \\ 0 & (\varkappa = 3, 4, 5). \end{cases} \tag{55.15}$$

In heating the plate is usually compressed at the edges, the stresses there equal $\sigma'_\varkappa(\pm a) = -d'_{\varkappa\lambda}\alpha'_\lambda ha^2/(3k'_3)$, and extended in the middle; in the middle plane of the plate the stresses equal $\sigma'_\varkappa(0) = d'_{\varkappa\lambda}\alpha'_\lambda ha^2/(6k'_3)$. In cooling the plate $h < 0$, therefore all the stresses are opposite to those developed during heating.*

The coefficients $\gamma'_\varkappa = d'_{\varkappa\lambda}\alpha'_\lambda$ for crystal plates of different orientations are given in Table 55.1. In dimensionality and even by the order of magnitude they coincide with the thermoelasticity coefficients $\beta'_\varkappa$ (see Sec. 51), but they differ from them numerically since $d'_{\varkappa\lambda}$ are not equal to coefficients $c_{\varkappa\lambda}$. When using this Table it should be borne in mind that coefficients $\gamma'_\varkappa$ are referred to the $X'_1X'_2X'_3$

* The problem has also been solved of the thermoelastic stresses developing under uniform heating of crystal cylinders, see Sirotin (1956).

Thermoela tic Coefficients $\gamma'_\varkappa$ for Crystal Plates

Systems and classes	Orientation of plate and choice of axes X'_1, X'_2	Coefficients $\gamma'_\varkappa$ related to the special system of coordinates X'_1, Y'_1, Z'_1
Triclinic system	$X'_3 \parallel X_3 \perp (001)$ $X'_1 \parallel X_1$ $X'_2 \parallel X_2$	$\gamma'_1 = A_1 [(s_{22}s_{66} - s_{26}^2)\alpha_1 + (s_{16}s_{26} - s_{66}s_{12})\alpha_2 + (s_{12}s_{26} - s_{22}s_{16})\alpha_6]$, $\gamma'_2 = A_1 [(s_{16}s_{26} - s_{12}s_{66})\alpha_1 + (s_{11}s_{66} - s_{16}^2)\alpha_2 + (s_{12}s_{16} - s_{11}s_{26})\alpha_6]$, $\gamma'_6 = A_1 [(s_{12}s_{26} - s_{22}s_{16})\alpha_1 + (s_{12}s_{16} - s_{11}s_{26})\alpha_2 + (s_{11}s_{22} - s_{12}^2)\alpha_6]$; $1/A_1 = s_{11}s_{22}s_{66} + 2s_{12}s_{16}s_{26} - s_{11}s_{26}^2 - s_{22}s_{16}^2 - s_{66}s_{12}^2$.
	$X'_3 \parallel X_1$ $X'_1 \parallel X_3$ $X'_2 \parallel X_2$	$\gamma'_1 = A_2 [(s_{22}s_{44} - s_{24}^2)\alpha_3 + (s_{24}s_{34} - s_{44}s_{23})\alpha_2 + (s_{23}s_{24} - s_{22}s_{34})\alpha_4]$, $\gamma'_2 = A_2 [(s_{24}s_{34} - s_{44}s_{23})\alpha_3 + (s_{33}s_{44} - s_{34}^2)\alpha_2 + (s_{23}s_{34} - s_{33}s_{24})\alpha_4]$; $\gamma'_6 = A_2 [(s_{23}s_{24} - s_{22}s_{34})\alpha_3 + (s_{23}s_{34} - s_{33}s_{24})\alpha_2 + (s_{22}s_{33} - s_{23}^2)\alpha_4]$; $1/A_2 = s_{22}s_{33}s_{44} + 2s_{23}s_{34}s_{24} - s_{22}s_{34}^2 - s_{33}s_{24}^2 - s_{44}s_{23}^2$.
	$X'_3 \parallel X_2$ $X'_1 \parallel X_1$ $X'_2 \parallel X_3$	$\gamma'_1 = A_3 [(s_{33}s_{55} - s_{35}^2)\alpha_1 + (s_{15}s_{35} - s_{55}s_{13})\alpha_3 + (s_{13}s_{35} - s_{33}s_{15})\alpha_5]$, $\gamma'_2 = A_3 [(s_{15}s_{35} - s_{55}s_{13})\alpha_1 + (s_{11}s_{35} - s_{15}^2)\alpha_3 + (s_{13}s_{15} - s_{11}s_{35})\alpha_5]$, $\gamma'_6 = A_3 [s_{13}s_{35} - s_{33}s_{15})\alpha_1 + (s_{13}s_{15} - s_{11}s_{35})\alpha_3 + (s_{11}s_{33} - s_{13}^2)\alpha_5]$; $1/A_3 = s_{11}s_{33}s_{55} + 2s_{13}s_{15}s_{35} - s_{11}s_{35}^2 - s_{33}s_{15}^2 - s_{55}s_{13}^2$.
Monoclinic system	$X'_3 \parallel X_2 \perp (010)$ $X'_1 \parallel X_3 \parallel [001]$	$\gamma'_1 = A_3 [(s_{11}s_{55} - s_{15}^2)\alpha_3 + (s_{35}s_{15} - s_{55}s_{31})\alpha_1 + (s_{31}s_{15} - s_{11}s_{35})\alpha_5]$, $\gamma'_2 = A_3 [(s_{35}s_{15} - s_{55}s_{31})\alpha_3 + (s_{33}s_{55} - s_{35}^2)\alpha_1 + (s_{31}s_{35} - s_{33}s_{15})\alpha_5]$, $\gamma'_6 = A_3 [(s_{31}s_{15} - s_{11}s_{35})\alpha_3 + (s_{31}s_{35} - s_{33}s_{15})\alpha_1 + (s_{33}s_{11} - s_{31}^2)\alpha_5]$.
	$X'_3 \parallel X_3 \parallel [001]$ $X'_2 \parallel X_2 \parallel [010]$	$\gamma'_1 = A_4 (s_{22}\alpha_1 - s_{12}\alpha_2)$, $\gamma'_2 = A_4 (-s_{12}\alpha_1 + s_{11}\alpha_2)$. $\gamma'_6 = 0$; $1/A_4 = s_{11}s_{22} - s_{12}^2$.

	$X_3' \perp (001)$ $X_2' \parallel X_2 \parallel [010]$ $\varphi = \beta - 90°$	$\gamma_1' = A_5 [(s_{22}\alpha_1 - s_{12}\alpha_2) \cos^2\varphi + (s_{22}\alpha_3 - s_{23}\alpha_2) \sin^2\varphi - (s_{22}\alpha_5 - s_{25}\alpha_2) \sin\varphi \cos\varphi]$, $\gamma_2' = A_5 \{(s_{11}\alpha_2 - s_{12}\alpha_1) \cos^4\varphi + (s_{33}\alpha_2 - s_{23}\alpha_3) \sin^4\varphi +$ $+ [(2s_{31} + s_{55}) \alpha_2 - s_{23}\alpha_1 - s_{12}\alpha_3 - s_{25}\alpha_5] \sin^2\varphi \cos^2\varphi + (s_{25}\alpha_1 - s_{15}\alpha_2 +$ $+ s_{12}\alpha_5) \cos^3\varphi \sin\varphi + (-s_{35}\alpha_2 + s_{25}\alpha_3 + s_{23}\alpha_5) \cos\varphi \sin^3\varphi\}$, $\gamma_6' = 0$; $1/A_5 = (s_{11}s_{22} - s_{12}^2) \cos^4\varphi + (s_{22}s_{33} - s_{23}^2) \sin^4\varphi +$ $+ (2s_{22}s_{31} - 2s_{12}s_{23} + s_{22}s_{55} - s_{25}^2) \cos^2\varphi \sin^2\varphi -$ $- [(s_{22}s_{15} - s_{12}s_{25}) \cos^2\varphi + (s_{22}s_{35} - s_{23}s_{25}) \sin^2\varphi] \sin 2\varphi$.
Rhombic system	$X_3' \parallel X_3 \perp (001)$ $X_1' \parallel X_1 \parallel [100]$	$\gamma_1' = A_4 (s_{22}\alpha_1 - s_{12}\alpha_2)$, $\gamma_2' = A_4 (-s_{12}\alpha_1 + s_{11}\alpha_2)$, $\gamma_6' = 0$; $1/A_4 = s_{11}s_{22} - s_{12}^2$.
	$X_3' \perp (h0l)$ $X_2' \parallel X_2 \parallel [010]$	$\gamma_1' = A_6 [h^2 (c/a)^2 + l^2] [l^2 (s_{22}\alpha_1 - s_{12}\alpha_2) + h^2 (c/a)^2 (s_{22}\alpha_3 - s_{23}\alpha_2)]$, $\gamma_2' = A_6 \{l^4 (s_{11}\alpha_2 - s_{12}\alpha_1) + h^4 (c/a)^4 (s_{33}\alpha_2 - s_{23}\alpha_3) -$ $- h^2 l^2 (c/a)^2 [s_{23}\alpha_1 + s_{12}\alpha_3 - (2s_{31} + s_{35}) \alpha_2]\}$, $\gamma_6' = 0$. $1/A_6 = l^4 (s_{11}s_{22} - s_{12}^2) + h^4 (c/a)^4 (s_{22}s_{33} - s_{23}^2) + h^2 l^2 (c/a)^2 (2s_{22}s_{31} - 2s_{12}s_{23} + s_{22}s_{55})$.
Trigonal system	$X_3' \parallel X_3 \perp (0001)$	$\gamma_1' = \gamma_2' = \alpha_1/(s_{11} + s_{12})$, $\gamma_6' = 0$.
All classes	$X_3' \parallel X_1 \perp (2\bar{1}\bar{1}0)$ $X_1' \parallel X_3 \parallel [0001]$ $X_2' \parallel X_2 \parallel [01\bar{1}0]$	$\gamma_1' = A_7 [-s_{44}s_{13}\alpha_1 + (s_{11}s_{44} - s_{14}^2) \alpha_3]$, $\gamma_2' = A_7 (s_{33}s_{44}\alpha_1 - s_{44}s_{13}\alpha_3)$, $\gamma_6' = A_7 s_{14} (s_{33}\alpha_1 - s_{13}\alpha_3)$; $1/A_7 = s_{44} (s_{11}s_{33} - s_{13}^2) - s_{33}s_{14}^2$.
Classes 3 and $\bar{3}$	$X_3' \parallel X_2 \perp (01\bar{1}0)$ $X_1' \parallel X_1 \parallel [2\bar{1}\bar{1}0]$ $X_2' \parallel X_3 \parallel [0001]$	$\gamma_1' = A_8 s_{44} (s_{33}\alpha_1 - s_{13}\alpha_3)$, $\gamma_2' = A_8 [-s_{44}s_{13}\alpha_1 + (s_{11}s_{41} - s_{25}^2) \alpha_3]$, $\gamma_6' = A_8 s_{25} (s_{33}\alpha_1 - s_{13}\alpha_3)$; $1/A_8 = s_{44} (s_{11}s_{33} - s_{13}^2) - s_{33}s_{25}^2$.

Table 55.1 (cont'd)

Systems and classes	Orientation of plate and choice of axes X_1', X_2'	Coefficients $\gamma_\varkappa'$ related to the special system of coordinates X_1', Y_1', Z_1'
Classes 32, $3m$, $\bar{3}m$	$X_3' \parallel X_2 \perp (01\bar{1}0)$ $X_1' \parallel X_1 \parallel [2\bar{1}\bar{1}0]$ $X_2' \parallel X_3 \parallel [0001]$	$\gamma_1' = A_9 (s_{33}\alpha_1 - s_{13}\alpha_3)$, $\gamma_2' = A_9 (-s_{13}\alpha_1 + s_{11}\alpha_3)$, $\gamma_6' = 0$, $1/A_9 = s_{11}s_{33} - s_{13}^2$.
Hexagonal system and textures	$X_3' \parallel X_3 \perp (0001)$	$\gamma_1' = \gamma_2' = \alpha_1/(s_{11} + s_{12})$, $\gamma_6' = 0$.
	$X_3' \perp X_3$ $X_1' \perp X_3$, X_2', $\parallel X_3$	$\gamma_1' = A_9 (s_{33}\alpha_1 - s_{13}\alpha_3)$, $\gamma_2' = A_9 (-s_{13}\alpha_1 + s_{11}\alpha_3)$, $\gamma_6' = 0$; $1/A_9 = s_{11}s_{33} - s_{13}^2$.
Tetragonal system	$X_3' \parallel X_3 \perp (001)$	$\gamma_1' = \gamma_2' = \alpha_1/(s_{11} + s_{12})$, $\gamma_6' = 0$.
	$X_3' \parallel X_1 \perp (100)$ $X_1' \parallel X_2 \parallel [010]$ $X_2' \parallel X_3 \parallel [001]$	$\gamma_1' = A_9 (s_{33}\alpha_1 - s_{13}\alpha_3)$, $\gamma_2' = A_9 (-s_{13}\alpha_1 + s_{11}\alpha_3)$, $\gamma_6' = 0$; $1/A_9 = s_{11}s_{33} - s_{13}^2$.
All classes	$X_3' \perp (110)$ $X_1' \perp [1\bar{1}0]$ $X_2' \parallel X_3 \parallel [001]$	$\gamma_1' = 4A_{10} (s_{33}\alpha_1 - s_{13}\alpha_3)$, $\gamma_2' = A_{10} [-4s_{13}\alpha_1 + (2s_{11} + 2s_{12} + s_{66})\alpha_3]$, $\gamma_6' = 0$; $1/A_{10} = s_{33}(2s_{11} + 2s_{12} + s_{66}) - 4s_{13}^2$.
Classes 422, $4mm$, $42m$, $4/mmm$	$X_3' \perp (h0l)$ $X_2' \parallel X_2 \parallel [010]$	$\gamma_1' = A_{11} [h^2 (c/a)^2 + l^2] [l^2 (s_{11} - s_{12})\alpha_1 + h^2 (c/a)^2 (s_{11}\alpha_3 - s_{13}\alpha_1)]$, $\gamma_2' = A_{11} \{l^4 (s_{11} - s_{12})\alpha_1 + h^4 (c/a)^4 s_{33}\alpha_1 - s_{13}\alpha_3) +$ $+ h^2 l^2 (c/a)^2 [(s_{13} + s_{44})\alpha_1 - s_{12}\alpha_3]\}$ $\gamma_6' = 0$; $1/A_{11} = l^4 (s_{11}^2 - s_{12}^2) + h^4 (c/a)^4 (s_{11}s_{33} - s_{13}^2) + h^2 l^2 (c/a)^2 (2s_{11}s_{13} - 2s_{12}s_{13} + s_{11}s_{44})$.

	$X_3' \perp (hhl)$ $X_2' \parallel [1\bar{1}0]$	$\gamma_1' = A_{12}\,[2h^2 (c/a)^2 + l^2]\,\{l^2 s_{66}\alpha_1 + h^2 (c/a)^2 [2s_{11} + 2s_{12} + s_{66})\,\alpha_3 - 4s_{13}\alpha_1]\}$, $\gamma_2' = A_{12}\,\{l^4 s_{66}\alpha_1 + 8h^4 (c/a)^4 (s_{33}\alpha_1 - s_{13}\alpha_3) +$ $+ h^2 l^2 (c/a)^2 [4\,(s_{13} + s_{44})\,\alpha_1 - (2s_{11} + 2s_{12} - s_{66})\,\alpha_3]\}$ $\quad \gamma_6' = 0$; $1/A_{12} = l^4 s_{66}\,(s_{11} + s_{12}) + 2h^4 (c/a)^4 (2s_{11}s_{33} + 2s_{12}s_{33} + s_{66}s_{33} - 4s_{13}^2) +$ $+ h^2 l^2 (c/a)^2 (4s_{66}s_{13} + 2s_{11}s_{44} + 2s_{12}s_{44} + s_{66}s_{44})$,
Cubic system	$X_3' \perp (001)$	$\gamma_1' = \gamma_2' = \alpha/(s_{11} + s_{12})$, $\quad \gamma_6' = 0$.
	$X_3' \perp (110)$ $X_1' \parallel [1\bar{1}0]$, $X_2' \parallel [001]$	$\gamma_1' = 4A_{13}\,(s_{13} - s_{12})\,\alpha$, $\quad \gamma_2' = A_{13}\,(2s_{11} - 2s_{12} + s_{44})\,\alpha$, $\quad \gamma_6' = 0$; $1/A_{13} = s_{11}\,(2s_{11} + 2s_{12} + s_{44}) - 4s_{12}^2$.
	$X_3' \perp (111)$	$\gamma_1' = \gamma_2' = 6\alpha/(4s_{11} + 8s_{12} + s_{44})$, $\quad \gamma_6' = 0$.
	$X_3' \perp (h0l)$ $X_1' \parallel [010]$	$\gamma_1' = A_{14}\,(h^2 + l^2)^2\,(s_{11} - s_{12})\,\alpha$, $\quad \gamma_2' = A_{14}\,[(h^4 + l^4)\,(s_{11} - s_{12}) +$ $+ h^2 l^2 s_{44}]\,\alpha$, $\quad \gamma_6' = 0$; $1/A_{14} = (h^4 + l^4)\,(s_{11}^2 - s_{12}^2) + h^2 l^2\,(2s_{11}s_{12} - 2s_{12}^2 + s_{11}s_{44})$.
	$X_3' \perp (hhl)$ $X_1' \parallel [1\bar{1}0]$	$\gamma_1' = A_{15}\,(2h^2 + l^2)\,[l^2 s_{44} + h^2\,(2s_{11} - 2s_{12} + s_{44})]\,\alpha$, $\gamma_2' = A_{15}\,[l^4 s_{44} + 8h^4\,(s_{11} - s_{12}) + h^2 l^2\,(5s_{44} - 2s_{11} + 2s_{12})]\,\alpha$, $\quad \gamma_6' = 0$; $1/A_{15} = l^4\,(s_{11} + s_{12})\,s_{44} + 2h^4\,[(2s_{11} + 2s_{12} + s_{44})\,s_{11} - 4s_{22}^2] +$ $+ h^2 l^2\,(2s_{11} + 6s_{12} + s_{44})\,s_{44}$.
Isotropic bodies		$\gamma_1' = \gamma_2' = \alpha_1/(s_{11} + s_{12}) = \alpha E/(1 - \nu)$, $\quad \gamma_6' = 0$.

Notation. a, c, β are the parameters of crystal lattice. h, l are Miller indices, E is Young's modulus, ν is Poisson's ratio.

special system of coordinates connected with the plate, therefore they are denoted with a prime. Coefficients $s_{\lambda u}$ and α_λ are referred to the crystal-physical system of coordinates, this allowing an immediate substitution of their tabulated values into formulas above.

In general, the thermoelasticity of anisotropic bodies is discussed in the work of Uzdalev (1967).

Sec. 56. Elastic Waves in Crystals

The propagation of elastic (acoustic and ultrasonic) waves in crystals differs by a number of features from their propagation in isotropic bodies. The distinctions resemble to a certain degree the distinctions between the propagation of light in crystals and in isotropic bodies.

A plane elastic wave (whether in a crystal or in an isotropic medium) is described by the field of the displacement vector

$$\boldsymbol{u}(\boldsymbol{r}, t) = A\boldsymbol{p} \exp(i\boldsymbol{k}\cdot\boldsymbol{r} - i\omega t). \tag{56.1}$$

Here A is the wave amplitude, $\boldsymbol{p}$ is the polarization vector, i.e. a unit vector coinciding in direction with the displacement vector, $\boldsymbol{k} = (2\pi/\lambda)\,\boldsymbol{m}$ is the wave vector, $\omega = (2\pi/\lambda)\,v$ is the cyclic frequency, λ is the wavelength, v is the phase velocity, $\boldsymbol{m}$ is the unit vector of the wave normal. Actual displacements are equal to the real part of this complex expression. Formula (56.1) can be conveniently rewritten as

$$\boldsymbol{u}(\boldsymbol{r}, t) = A\boldsymbol{p} \exp[(2\pi i/\lambda)(\boldsymbol{m}\cdot\boldsymbol{r} - vt)]. \tag{56.2}$$

The field of displacements must satisfy the equations of elastodynamics

$$c_{ijkl}\frac{\partial^2 u_l}{\partial x_j\,\partial x_k} = \rho\frac{\partial^2 u_i}{\partial t^2}$$

where c_{ijkl} are the adiabatic coefficients of the crystal's elasticity, ρ is its density. Substituting expression (56.2) into equation (56.1) and noting that in case of exponential functions of the form (56.2) the differentiation with respect to t reduces to multiplication by $-(2\pi i/\lambda)\,v$, and with respect to x_j, by $(2\pi i/\lambda)\,m_j$, we obtain the principal equation of the theory of elastic waves in crystals—*the Christoffel equation*

$$c_{ijkl}m_j m_k p_l = \rho v^2 p_i. \tag{56.3}$$

Taking into account the internal symmetry of tensor $\mathbf{c}$, we introduce a symmetric *Christoffel tensor*

$$M_{il} = c_{ijkl}m_j m_k, \quad \mathbf{M} = \boldsymbol{m}\cdot\mathbf{c}\cdot\boldsymbol{m}. \tag{56.4}$$

Since tensor $\mathbf{M}$ depends not only on the matter tensor $\mathbf{c}$ but also on the direction of the wave propagation, it is not a matter tensor and

therefore its external symmetry can be lower than the crystal symmetry*. Substituting this tensor into (56.3), we shall have the Christoffel equation in the following form:

$$M_{il}p_l = \rho v^2 p_i, \quad \mathbf{M}\cdot\boldsymbol{p} = \rho v^2 \boldsymbol{p}. \tag{56.5}$$

Use is often made of the reduced tensor of the coefficients of elasticity $\lambda_{ijkl} = c_{ijkl}/\rho$ and the reduced Christoffel tensor $\Lambda_{il} = \lambda_{ijkl}m_j m_k$. In this case the Christoffel equations take the form:

$$\Lambda_{il}p_l = v^2 p_i. \tag{56.5'}$$

The Christoffel equations show that polarization vectors $\boldsymbol{p}$ of the elastic waves propagating in a crystal in the direction $\boldsymbol{m}$ are the eigenvectors of the Christoffel tensor $\mathbf{M}(\boldsymbol{m})$ or $\Lambda(\boldsymbol{m})$. If the Christoffel tensor $\mathbf{M}(\boldsymbol{m})$ has three different eigenvalues, then in a given direction $\boldsymbol{m}$ there can propagate three isonormal mutually perpendicular elastic waves, the phase velocity v_k of each of them being defined by the eigenvalue** $\rho v^2_{(k)}$ corresponding to the given eigenvector $\boldsymbol{p}_{(k)}$ (the eigenvalues of the reduced Christoffel tensor Λ_{il} are equal to the squares of phase velocities $v^2_{(k)}$). The fact that waves of strictly definite polarization alone can propagate across a crystal makes crystal acoustics akin to crystal optics. In distinction from electromagnetic waves three elastic waves, and not two, propagate in the given direction $\boldsymbol{m}$. The wave whose polarization vector makes up the smallest angle with the wave normal vector is called *quasilongitudinal* wave, the other two waves are *quasitransversal*. It may happen that the polarization vector of one of the waves coincides with the wave-normal vector, then this wave is longitudinal, the other two waves in this case being always transversal. Such a direction $\boldsymbol{m}$ is called the *longitudinal normal*. It may happen that only one wave is transversal; in this case the angle between the polarization vector of the quasilongitudinal wave and the wave normal is equal to the angle between the polarization vector of the quasitransversal wave and the wave-front plane. In this case $\boldsymbol{m}$ is the *transversal normal*.

If two eigenvalues of tensor $\mathbf{M}(\boldsymbol{m})$ coincide, then in the direction $\boldsymbol{m}$ can propagate a quasilongitudinal wave with a polarization vector $\boldsymbol{p}_{(0)}$, whose phase velocity $v_{(0)}$ is defined by the single eigenvalue $\rho v^2_{(0)}$, and a large number of quasitransversal waves with the same

* For the formulas defining the Christoffel tensor for each elastic symmetry class see F. I. Fedorov (1965).

** The eigenvalues of the Christoffel tensors are positive at any $\boldsymbol{m}$; this is due to inequalities which are satisfied by tensor $\mathbf{c}$, see Sec. 63. For the proof of the positiveness of the eigenvalues of the Christoffel tensor see F. I. Fedorov (1965).

velocities $v_{(1)}$ whose polarization vectors have all possible directions perpendicular to $\boldsymbol{p}_{(0)}$. One of these waves is purely transversal; its polarization vector is $\boldsymbol{p}_{(1)} \parallel (\boldsymbol{p}_{(0)} \times \boldsymbol{m})$. In this case direction $\boldsymbol{m}$ is called *the acoustic axis.* If, in addition, $\boldsymbol{m}$ happens to be also a longitudinal normal, i.e. $\boldsymbol{p}_{(0)} = \boldsymbol{m}$, then all the waves polarized perpendicularly to $\boldsymbol{p}_{(0)}$ are transversal and the direction is called the *longitudinal acoustic axis* (see Khatkevich, 1962).

To compute the elastic wave phase velocity it is necessary to find the corresponding eigenvalue of Christoffel tensor. This painstaking method is required only when the direction of the polarization vector $\boldsymbol{p}$ is unknown. If it is known, the wave velocity is easily computed as

$$v = \sqrt{\frac{1}{\rho}\, \boldsymbol{pm} : \mathbf{c} : \boldsymbol{mp}} = \sqrt{\frac{1}{\rho}\, c_{ijkl} p_i m_j m_k p_l}, \tag{56.6}$$

which can be written in the form convenient for computations

$$v = \sqrt{\frac{1}{\rho}\, c_{\lambda\mu} L_\lambda L_\mu}, \tag{56.7}$$

where

$$c_{\lambda\mu} = c_{ijkl} \quad (i,\ j \leftrightarrow \lambda = 1,\ \ldots,\ 6;\quad k,\ l \leftrightarrow \mu = 1,\ \ldots,\ b),$$

$$L_\lambda = \begin{cases} p_i m_j & (ij \leftrightarrow \lambda = 1,\ 2,\ 3), \\ p_i m_j + m_i p_j & (ij \leftrightarrow \lambda = 4,\ 5,\ 6). \end{cases}$$

In particular, the phase velocity of the longitudinal wave

$$v = \sqrt{\frac{1}{\rho}\, c_{\lambda\mu} N_\lambda N_\mu} \tag{56.8}$$

where

$$N_\lambda = \begin{cases} m_i m_j & (ij \leftrightarrow \lambda = 1,\ 2,\ 3), \\ 2 m_i m_j & (ij \leftrightarrow \lambda = 4,\ 5,\ 6). \end{cases}$$

The derivation of formulas (56.7) and (56.8) is given in Appendix F. It should be remembered that to use (56.7) it is necessary to be sure that the given vectors $\boldsymbol{m}$ and $\boldsymbol{p}$ can serve as the wave normal and the polarization vector of one and the same elastic wave respectively. Similarly, formula (56.8) can be used only when it is certain that $\boldsymbol{m}$ is the longitudinal normal of the given crystal.

When an elastic wave propagates in an anisotropic medium, the energy flow, generally speaking, diverges from the wave normal.

The velocity and direction of the energy flow are characterized

by a *beam*, or group, *velocity** vector

$$\boldsymbol{\omega} = \frac{\partial \omega}{\partial \boldsymbol{k}}, \quad w_i = \frac{\partial \omega}{\partial k_i}. \tag{56.9}$$

In order to relate the beam velocity to other characteristics of the elastic wave, we multiply both sides of the Christoffel equation (56.3) scalarly by the polarization vector $\boldsymbol{p}$ and obtain the equality

$$c_{ijkl} p_i m_j m_k p_l = \rho v^2, \quad \boldsymbol{pm} : \mathbf{c} : \boldsymbol{mp} = \rho v^2. \tag{56.10}$$

Upon multiplication of both its sides by $4\pi^2/\lambda^2$, we can write it as

$$c_{ijlm} p_i k_j k_l p_m = \rho \omega^2, \quad \boldsymbol{pk} : \mathbf{c} : \boldsymbol{kp} = \rho \omega^2. \tag{56.11}$$

Having differentiated (56.11) with respect to $\boldsymbol{k}$, we find

$$\boldsymbol{p} \cdot \mathbf{c} : \boldsymbol{kp} + \boldsymbol{pk} : \mathbf{c} \cdot \boldsymbol{p} = 2\rho\omega \frac{\partial \omega}{\partial \boldsymbol{k}}.$$

Hence, with the aid of equation (56.9) and the internal symmetry of tensor $\mathbf{c}$ we find the beam velocity

$$w_j = \frac{1}{\rho\omega} c_{ijlm} p_i p_m k_l, \quad \boldsymbol{\omega} = \frac{1}{\rho\omega} (\boldsymbol{p} \cdot \mathbf{c} \cdot \boldsymbol{p}) \cdot \boldsymbol{k};$$

which is more conveniently presented as a function of v and $\boldsymbol{m}$:

$$w_j = \frac{1}{\rho v} c_{ijkl} p_i p_l m_k, \quad \boldsymbol{\omega} = \frac{1}{\rho v} (\boldsymbol{p} \cdot \mathbf{c} \cdot \boldsymbol{p}) \cdot \boldsymbol{m}. \tag{56.12}$$

We shall call a symmetric second-rank tensor

$$P_{jk} = c_{ijkl} p_i p_l, \quad \mathbf{P} = \boldsymbol{p} \cdot \mathbf{c} \cdot \boldsymbol{p} \tag{56.13}$$

the second Christoffel tensor. Substituting it into (56.12), we find

$$w_j = \frac{1}{\rho v} P_{jk} m_k, \quad \boldsymbol{\omega} = \frac{1}{\rho v} \mathbf{P} \cdot \boldsymbol{m}. \tag{56.14}$$

If the direction of the elastic wave beam velocity coincides with the wave normal, we shall call this wave (by analogy with crystal optics) an *ordinary* wave in the opposite case—*an extraordinary* one. From the equation (56.14) it is clear that an elastic wave is an ordinary wave when, and only when the wave normal vector $\boldsymbol{m}$

---

* Expressions (56.9) are more conveniently written in the form $\omega = \frac{\partial V}{\partial \boldsymbol{m}}$, $\omega_i = \frac{dV}{dm_i}$, but these relations lose their meaning for those directions of the wave normal $\boldsymbol{m}$ for which $\frac{\partial V}{\partial \boldsymbol{m}} = 0$. Since in this case $\frac{\partial \omega}{\partial \boldsymbol{k}} = v\boldsymbol{m}$, the group velocity is defined for these directions too. So, in the directions in which $\frac{\partial V}{\partial \boldsymbol{m}} = 0$, the group velocity coincides with the phase velocity. The waves for which $\omega = vm$ are called *ordinary* waves (see below).

is the eigenvector of Christoffel second tensor **P**. All the longitudinal waves, for instance, are ordinary waves. Indeed, for a longitudinal wave $\boldsymbol{m}$ is a vector of polarization, and for this reason it is the eigenvector of Christoffel first tensor $\boldsymbol{M}$; however for the same reason the two Christoffel tensors coincide in a longitudinal wave, so that $\boldsymbol{m}$ is also the eigenvector of the second Christoffel tensor **P**.

It is evident geometrically that the projection of the beam velocity vector onto the direction of the wave normal is equal to the phase velocity. This is also easily derived analytically. By scalar multiplication of both sides of relation (56.12) by the unit vector of the wave normal $\boldsymbol{m}$ and taking (56.10) into account we obtain

$$\boldsymbol{w}\cdot\boldsymbol{m} = v. \tag{56.15}$$

So, the beam velocity is equal to the phase velocity only in an ordinary wave; in an extraordinary wave it exceeds the phase velocity, the greater the divergence of the energy flow from the wave normal, the higher is the beam velocity. The angle ψ between the energy flow and the wave normal is defined by the relation

$$\cos\psi = \boldsymbol{m}\cdot\boldsymbol{s}, \tag{56.16}$$

where $\boldsymbol{s} = \boldsymbol{\omega}/\omega$ is the unit vector of the beam. We find $\boldsymbol{\omega}/\omega$ from (56.14) and, having scalarly multiplied it by $\boldsymbol{m}$, we obtain

$$\cos\psi = \frac{\boldsymbol{m}\cdot\mathbf{P}\cdot\boldsymbol{m}}{\sqrt{\boldsymbol{m}\cdot\mathbf{P}\cdot\mathbf{P}\cdot\boldsymbol{m}}} = \frac{\rho v^2}{\sqrt{P_{ij}P_{ik}m_jm_k}} \tag{56.17}$$

It should be borne in mind that the divergence of the beam from the wave normal sometimes attains tens of degrees (see Figs. 56.6, 56.8, 56.11, 56.14, 56.16), so that it must not be neglected. In general, the anisotropy of crystals is much more apparent in crystal acoustics than in crystal optics, especially in visible light (in the infrared light the anisotropy of the optical properties of crystals is displayed somewhat stronger than in the visible light).

In the direction $\boldsymbol{m}$, which is not an acoustic axis, there can propagate three mutually perpendicular polarized waves with polarization vectors $\boldsymbol{p}_{(0)}$, $\boldsymbol{p}_{(1)}$, $\boldsymbol{p}_{(2)}$ and phase velocities $v_{(0)}$, $v_{(1)}$, $v_{(2)}$. To each of them there corresponds a beam velocity vector $\boldsymbol{w}_{(i)} = (\rho v_{(i)})^{-1}\mathbf{P}_{(i)}\,\boldsymbol{m}$. In the direction of the acoustic axis besides a quasilongitudinal wave $\{\boldsymbol{m}, \boldsymbol{p}_{(0)}\}$ a great number of quasitransversal waves $\{\boldsymbol{m}, \boldsymbol{p}_{(\varphi)}\}$ can propagate where φ is the angle reckoned from a certain direction in the proper plane of tensor **M**.
Many beams

$$\boldsymbol{w}_{(\varphi)} = \frac{1}{\rho v_{(1)}}\mathbf{P}_{(\varphi)}\cdot\boldsymbol{m} \tag{56.18}$$

correspond to these waves.

These beams obviously form a certain cone, and the whole picture is an acoustical analogue of the phenomenon of crystal optics known as *internal conical refraction* (see Sec. 39)*.

Let us consider, for instance, an elastic wave propagating in a crystal of the trigonal system along its principal symmetry axis: $\boldsymbol{m} = \boldsymbol{e}_3$. Then the Christoffel tensor $M_{il} = c_{i33l}$ so that for trigonal system crystals (see Table E.18)

$$\| M_{il} \| = \begin{Vmatrix} c_{44} & 0 & 0 \\ 0 & c_{44} & 0 \\ 0 & 0 & c_{33} \end{Vmatrix}.$$

This tensor has a single eigenvalue c_{33} which corresponds to an eigenvector $\boldsymbol{p}_{(0)} = \boldsymbol{e}_3 = \boldsymbol{m}$, i.e. to a longitudinal wave propagating with a velocity $v_{(0)} = \sqrt{c_{33}/\rho}$, and a double eigenvalue c_{44} corresponding to a set of eigenvectors

$$\boldsymbol{p}_{(\varphi)} = \boldsymbol{e}_1 \cos\varphi + \boldsymbol{e}_2 \sin\varphi,$$

i.e. to all the possible transversal waves ($\boldsymbol{p}_{(\varphi)} \perp \boldsymbol{m}$) propagating with a velocity $v_{(1)} = \sqrt{c_{44}/\rho}$. To each of such waves there corresponds the second Christoffel tensor

$$P_{il}^{(\varphi)} = c_{i11l} \cos^2\varphi + c_{i22l} \sin^2\varphi + (c_{i12l} + c_{i21l}) \sin\varphi \cos\varphi.$$

Taking into account the form of tensor **c** for a trigonal system crystal** we have

$$\| P_{il}^{(\varphi)} \| = \begin{Vmatrix} c_{11}\cos^2\varphi + c_{66}\sin^2\varphi & (c_{11} - c_{66})\cos\varphi\sin\varphi & 2c_{14}\sin\varphi\cos\varphi \\ (c_{11} - c_{66})\cos\varphi\sin\varphi & c_{11}\sin^2\varphi + c_{66}\cos^2\varphi & c_{14}(\cos^2\varphi - \sin^2\varphi) \\ 2c_{14}\cos\varphi\sin\varphi & c_{14}(\cos^2\varphi - \sin^2\varphi) & c_{44} \end{Vmatrix}.$$

Therefore each transversal wave with the polarization vector $\boldsymbol{p}_{(\varphi)}$ has its own beam velocity

$$\boldsymbol{w}_{(\varphi)} = \sqrt{c_{44}/\rho}\,[\boldsymbol{e}_3 + (c_{14}/c_{44})(\boldsymbol{e}_1 \sin 2\varphi + \boldsymbol{e}_2 \cos 2\varphi)]$$

Thus each beam makes up angle $\psi = \arctan(c_{14}/c_{44})$ with the direction of the wave normal $\boldsymbol{m} = \boldsymbol{e}_3$, and they all together form a circular cone. By the juxtaposition of the polarization and the direction of each beam, we obtain the corresponding distribution about the cone shown in Fig. 56.1.

---

* For details on internal conical refraction see Khatkevich (1962a); Alexandrov and Ryzhova (1964); Viswanathan (1969); Alexandrov (1975).

** Here, with the aid of relation $c_{11} - c_{12} = 2c_{66}$ we eliminate c_{12}. It is assumed that $c_{25} = 0$; for crystals of the higher subsystem this occurs already in the crystal-physical system of coordinates, while for the lower subsystem the same happens in the special system of coordinates (see Sec. 52).

Directions ⟨111⟩ in crystals of the cubic system are the three-fold symmetry axes, and about them the conical refraction of transversally polarized waves occurs. The divergence of beams from the wave normal in this case is

$$\psi = \arctan \frac{c_{11} - c_{12} - 2c_{44}}{\sqrt{2}\,(c_{11} - c_{12} + c_{44})}.$$

The conical refraction in crystal acoustics, in distinction from crystal optics, is not a minor effect; below we give the angle ψ for several crystals:

Trigonal:	sapphire $\psi = 9°05'$	quartz $17°10'$	calcite $30°45'$
Cubic:	NaCl $\psi = 8°45'$	silicon $12°40'$	fluorite $13°40'$

Elastic waves propagating along the directions related to the elements of the crystal's elastic symmetry can be longitudinal, transversal, ordinary and so on. The investigation of the possibilities arising therefrom is based on the coincidence of the symmetry axes of Christoffel tensors **M** and **P** with their eigenvectors while eigenvectors of tensor **M** (***m***) serve as polarization vectors of the elastic waves with normal ***m*** and the coincidence of one of the eigenvectors of tensor **P** (***p***) with wave normal ***m*** shows that the wave {***m***, ***p***} is an ordinary wave.

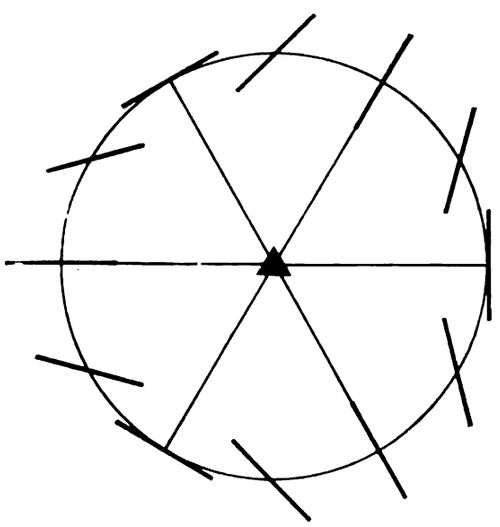


Fig. 56.1. The distribution of the polarization directions about a 3-fold symmetry axis under conical refraction. Symmetry planes are shown. The 2-fold axes should be imagined as lying below the plane of the paper (this is not a stereogram)

Tensor $\mathbf{M} = \boldsymbol{m}\cdot\mathbf{c}\cdot\boldsymbol{m}$ is defined by tensor **c** and dyad ***mm***; according to the Curie principle, among the symmetry elements of this tensor there are always such that are common for **c** and ***mm***:

$$G\,(\mathbf{N}) \supseteq G\,(\mathbf{c}) \cap G\,(\boldsymbol{mm}). \quad (56.19)$$

Groups G (**c**), i.e. the groups of the crystal elastic symmetry were listed in Sec. 52; the symmetry group of the dyad ***mm*** G (***mm***) $= \infty/mm$, the principal symmetry axis coinciding with the direction ***m***. For tensor **P** (***p***) we shall obtain similarly

$$G\,(\mathbf{P}) \supseteq G\,(\mathbf{c}) \cap G\,(\boldsymbol{pp}). \quad (56.20)$$

On the basis of these relations we shall analyze individual cases.

1. Let vector $\boldsymbol{m}$ coincide with one of the symmetry axes of the order $N > 2$. Then this axis will be a symmetry axis of the same order for tensor **M** too. But, since according to Hermann's theorem for a second-rank tensor, all the axes of the order greater than two serve as axes of an infinite order, tensor **M** will have the symmetry ∞/mm; two of its eigenvalues will coincide; one of its eigenvectors will be directed along the ∞ axis (i.e. in the direction of $\boldsymbol{m}$), the others will fill a plane perpendicular to it. Hence all the symmetry axes of the order $N > 2$ serve as longitudinal acoustic axes of the crystal. Elastic waves propagating along them are either longitudinal or transversal, being capable of any polarization the latter have the same velocities.

According to the general rule, the longitudinal waves are ordinary; the transversal waves call for particular investigation. In item 2 (see below) it is proved that transversal waves are ordinary already in the case the wave normal is directed along a two-fold symmetry axis. It is clear that this is also valid for a six-fold (infinite) and four-fold axes. Since in an isotropic body any direction can be an axis of an infinite order, all elastic waves in isotropic bodies have the same properties. The transversal waves, however, propagating along a three-fold symmetry axis are extraordinary, as was shown above.

2. Let vector $\boldsymbol{m}$ be directed along one of the two-fold symmetry axes of tensor **c**. This axis is a two-fold symmetry axis for tensor **M** too; this means that one of the tensor's eigenvectors is directed along it, and the two other eigenvectors are perpendicular to it. Thus the two-fold symmetry axes of tensor **c** are the longitudinal normals of the crystal but are not its acoustic axes. Along a two-fold axis there propagate together with a longitudinal wave two transversal waves with different phase velocities and strictly definite polarizations $\boldsymbol{p}_{(1)} \perp \boldsymbol{m}$ and $\boldsymbol{p}_{(2)} \perp \boldsymbol{m}$. If tensor **c** in addition to the $2 \parallel \boldsymbol{m}$ axis, has an even-fold symmetry axis perpendicular to it, then one of the transversal polarization vectors is directed along the even-fold axis; in this case the direction of the second transversal polarization vector too will be a two-fold axis for tensor **c**. If tensor **c** has no even-fold symmetry axes perpendicular to the $2 \parallel \boldsymbol{m}$ axis, then the direction of the transversal polarization vectors is defined by the elasticity coefficients of the crystal; this is the case, for example, in crystals of the trigonal and monoclinic systems.

We wish to emphasize that a two-fold symmetry axis for tensor **c** is not necessarily the same axis for the crystal; for instance, an m class crystal has no symmetry axes at all, but its tensor **c** along with a symmetry plane m has a two-fold axis* perpendicular to it;

* Let us note that any direction perpendicular to $\boldsymbol{m}$ is a two-fold symmetry axis for dyad $\boldsymbol{mm}$.

another example: crystals of the lower subsystems of the tetragonal and trigonal systems have no two-fold axes perpendicular to the principal symmetry axis, while their tensors **c** have such axes. At present we are particularly concerned with symmetry elements of tensor **c** and not with the symmetry elements of a crystal.

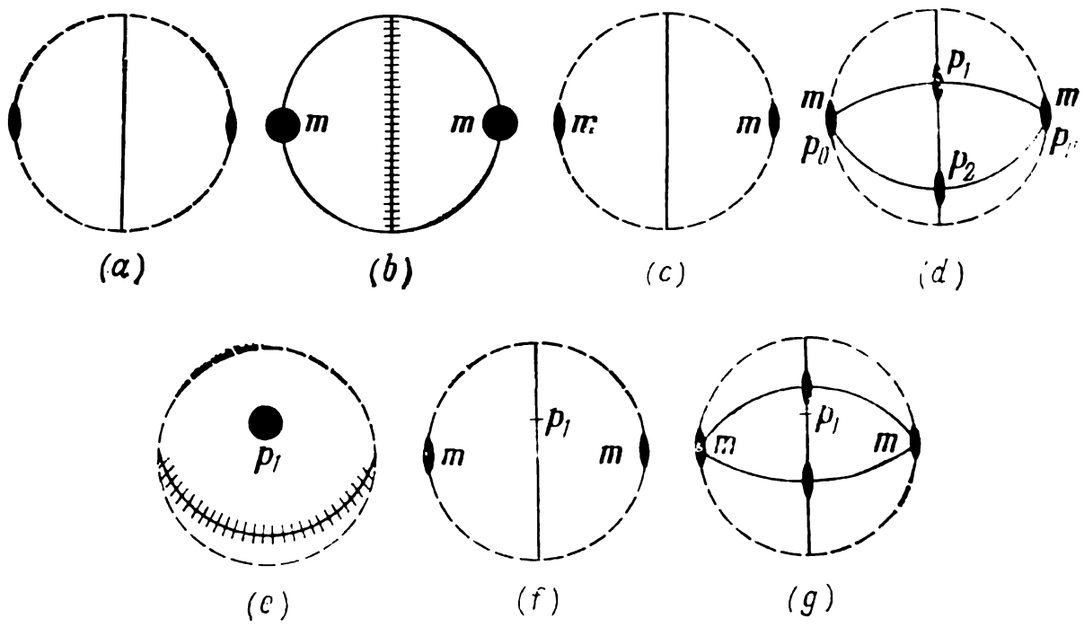


Fig. 56.2. Graphic proof of the propagation of a longitudinal and of two transversal elastic waves along the 2-fold symmetry axes; it is proved as well that not only the longitudinal wave but also the transversal waves are ordinary. (a) and (b) Stereograms of the elements of elastic symmetry G (c) and of the symmetry elements of a wave normal dyad G (mm) with account taken of their mutual array, (c) intersection of these groups; it is included in group G (M) of tensor M; (d) symmetry elements G (M); polarization vectors p_k are directed along the 2-fold axes, one of the vectors (p_0) coincides with m, a longitudinal wave corresponds to it; (e) symmetry elements G (p_1p_1); (f) intersection of groups G (p_1, p_1) and G (c); it is included in group G (P_1); (g) symmetry elements of tensor P_1; one of the 2-fold axes coincides with m, this proving that the wave [m, p_1] is an ordinary wave

Not only the longitudinal wave but also the two transversal waves are ordinary even in a general case when even-fold axes perpendicular to axis 2 || m are not included in G (c). This is because axis 2 || m is included in the intersections of groups G (c) $\cap$ $\cap$ G ($p_{(1)}p_{(1)}$) and G (c) $\cap$ G ($p_{(2)}p_{(2)}$) (Fig. 56.2) and therefore serves as the two-fold axis also for tensors **P** ($p_{(1)}$) and **P** ($p_{(2)}$).

3. Let vector m be perpendicular to a two-fold symmetry axis of tensor **c** or, which is just the same, lie in one of its symmetry planes. Then this two-fold symmetry axis will at the same time be a two-fold axis for dyad mm and, consequently for tensor **M** (m). This means that one of the tensor's eigenvectors coincides with the axis. But since his axis is perpendicular to vector m, the eigenvector

of tensor **M** directed along this axis is a polarization vector of a purely transversal wave. The other two polarization vectors are generally neither longitudinal nor transversal. Thus all the directions perpendicular to the two-fold axes of tensor **c** or lying in its planes of symmetry are transversal normals. In this case there are no reasons to expect that any of the waves (even a transversal one) will be ordinary.

Let us note that since all the even-fold symmetry axes are also two-fold axes, all the above arguments also hold for directions perpendicular to these axes, but certainly do not relate to directions perpendicular to three-fold axes.

4. Since the six-fold (infinite) and four-fold symmetry axes serve at the same time as two-fold axes, directions perpendicular to these axes are also transversal normals. But, in distinction from directions perpendicular to the two-fold symmetry axes, directions perpendicular to the six-fold (infinite) and four-fold axes have other remarkable properties. Evidently it will suffice to consider the directions lying in the plane (001) of a tetragonal system crystal. For these directions the vector of the wave normal can be represented in the form $\boldsymbol{m} = \boldsymbol{e}_1 \cos\varphi + \boldsymbol{e}_2 \sin\varphi$, and the Christoffel tensor becomes

$$M_{il} = c_{i11l}\cos^2\varphi + c_{i22l}\sin^2\varphi + (c_{i12l} + c_{i21l})\sin\varphi\cos\varphi.$$

For the tetragonal system crystals this gives

$$\| M_{il} \| = \begin{Vmatrix} c_{11}\cos^2\varphi + c_{66}\sin^2\varphi & (c_{12}+c_{66})\sin\varphi\cos\varphi & 0 \\ (c_{12}+c_{66})\sin\varphi\cos\varphi & c_{11}\sin^2\varphi + c_{66}\cos^2\varphi & 0 \\ 0 & 0 & c_{44} \end{Vmatrix}.$$

Hence it is clear that the direction of the polarization vector of a transversal wave $\boldsymbol{p}_{(1)} = \boldsymbol{e}_3$ and the velocity of this wave $v_{(1)} = \sqrt{c_{44}/\rho}$ do not depend on the direction of the wave normal with respect to plane (001), i.e. on angle φ. Thus plane (001) in crystals of the tetragonal system is isotropic with respect to elastic waves polarized perpedicularly to it: they all propagate with the same velocity. In crystals of the hexagonal system plane (0001) possesses the same property in crystals of the cubic system—all the planes of type {100}.

The second Christoffel tensor of such waves $P_{il} = c_{i33l}$ for a tetragonal system crystal takes the form

$$\| P_{il} \| = \begin{Vmatrix} c_{44} & 0 & 0 \\ 0 & c_{44} & 0 \\ 0 & 0 & c_{33} \end{Vmatrix}.$$

The coincidence of two of its eigenvalues shows that the whole plane X_1X_2, i.e. (001), is its proper plane. Thus vector $\boldsymbol{m}$ arbitrarily directed in an isotropic plane is an eigenvector of tensor **P** and,

consequently, the waves propagating in an isotropic plane and polarized perpendicularly to it are ordinary waves.

Above we considered all the cases when some direction in a crystal is a longitudinal normal, a transversal normal or an acoustic axis due to its peculiar position with respect to the symmetry elements of the elasticity coefficients tensor **c**. However this peculiar position is a sufficient, but not at all necessary condition for the given direction to be a longitudinal or a transversal normal or an acoustic axis. Actually, longitudinal normals, as was shown by F.I. Fedorov (1965), are available in any crystal irrespective of its symmetry. The proof of this is based on the fact that vector $\boldsymbol{m}$, if it is a longitudinal normal, is an eigenvector of tensor **M**, i.e. satisfies the equation

$$\boldsymbol{m}\cdot\mathbf{c}:\boldsymbol{mm}=\rho v^2\boldsymbol{m}, \quad c_{ijkl}m_jm_km_l=\rho v^2 m_i. \tag{56.21}$$

Let us now consider the function

$$F(\boldsymbol{m})=\boldsymbol{mm}:\mathbf{c}:\boldsymbol{mm}=c_{ijkl}m_im_jm_km_l, \tag{56.22}$$

where $\boldsymbol{m}$ is a unit vector:

$$f(\boldsymbol{m}) = 2(\boldsymbol{m}\cdot\boldsymbol{m}-1) = 2(m_im_i-1) = 0. \tag{56.23}$$

The function $F(\boldsymbol{m})$ is defined on the surface of a sphere $\boldsymbol{m}\cdot\boldsymbol{m}=1$ and, as any continuous function defined on a closed set, attains there its greatest and smallest values. At the corresponding values of $\boldsymbol{m}$ the equations of an extremum subject to constraints are satisfied

$$\begin{aligned}\frac{\partial}{\partial\boldsymbol{m}}(F-\lambda f)&=0,\\ \frac{\partial}{\partial m_i}(F-\lambda f)&=0.\end{aligned} \tag{56.24}$$

Substituting functions F and f defined by equations (56.22) and (56.23) into (56.24) we obtain exactly the equations of the longitudinal normal (56.21); the indefinite Lagrangian multiplier λ is found to be equal to ρv^2. Thus in any crystal there are at least two longitudinal normals: one of them corresponds to the greatest and the other to the smallest value of function F. Fig. 56.3 shows this function for a triclinic crystal of blue vitriol, longitudinal normals corresponding to its stationary points.

To find out if there is at least one acoustic axis in any crystal, it is first necessary to become acquainted with the *surface of phase velocities*. The surface is formed by the ends of all possible vectors of phase velocities $\boldsymbol{v}=v\boldsymbol{m}$, marked off from some point as from the centre of the surface. The equation of this surface

$$\det\|c_{ijkl}v_jv_k-\rho v^4\delta_{il}\|=0 \tag{56.25}$$

is obtained from the condition of the existence of non-zero solutions of Christoffel equations (56.3). Since (56.25) is an equation of the

12th degree it describes a surface of the 12th order*. As to each direction $\boldsymbol{m}$ there generally correspond three values v, the surface has three sheets. There can however be such directions $\boldsymbol{m}$ in which two of the three values of v coincide, and correspondingly two sheets of the phase velocities surface have a common point; just these directions are the acoustic axes (Figs. 56.4-56.15). The most widespread and until recently the only known configuration of the phase velocities surface, when the external sheet represents a quasilongitudinal wave and embraces two sheets of quasitransversal waves without touching them, is shown in Figs. 56.4*a*, 56.6*a*, 56.8*a* and *d*, 56.9*a*, 56.11, 56.12. In all these Figures the sheets of the quasitransversal waves have common points corresponding to the acoustic axes. In the majority of cases these are isolated directions: in hexagonal crystals ⟨0001⟩, in cubic crystals ⟨100⟩ and ⟨111⟩, but a beryl crystal has a whole cone of acoustic axes (its intersections with the plane of the section are shown in Fig. 56.6 by letters *D*).

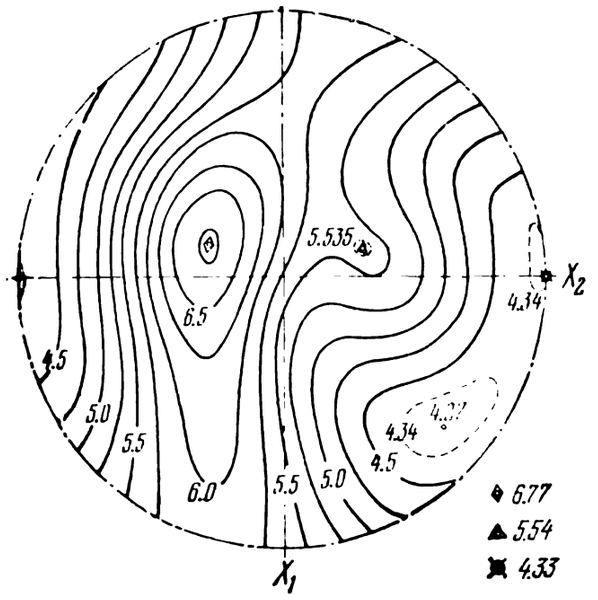


Fig. 56.3. Stereographic projection of the contour lines of function $F(m) = c_{ijkl}m_i m_l m_k m_l$ for a friclinic crystal of copper sulphate; in 10^{-13} N/m². Longitudinal waves propagate in the directions corresponding to the stationary points of: this function

The fact that with such a configuration of the phase velocities surface a crystal has, irrespective of its symmetry, at least one acoustic axis, follows from a general topological theorem: if $\boldsymbol{V}(\boldsymbol{m})$ is a continuous vector field tangential to sphere $\boldsymbol{m}\cdot\boldsymbol{m} = 1$ then there will be found at least one such value $\boldsymbol{m} = \boldsymbol{m}_0$ such that $\boldsymbol{V}(\boldsymbol{m}_0) = 0$ (Steenrod and Chinn, 1967). To each point of the phase velocities surface not lying on the acoustic axis a unit polarization vector of a corresponding wave is related: to the points of the external sheet—the vector of a quasilongitudinal wave, and to the points of the internal sheets that of a quasitransversal wave. Let us split each of these vector fields in two: a field $\boldsymbol{p}_{\parallel}^{(k)}(\boldsymbol{m})$ of vectors continuing corresponding vectors $\boldsymbol{v}^{(k)} = v_{(k)}\boldsymbol{m}$, and a field $\boldsymbol{p}_{\perp}^{(k)}(\boldsymbol{m})$ of vectors perpendicular to the corresponding vectors $\boldsymbol{v}^{(k)}$. Insofar as the external sheet makes no contacts with the internal ones, it is homeo-

* In special cases the degree of equation (56.25) and correspondingly the degree of the phase velocities surface can be considerably lower.

morphous (topologically equivalent) to a sphere, and the cited topological theorem shows once more that at least at one value of $\boldsymbol{m} = \boldsymbol{m}_0$ a tangential component of the quasilongitudinal wave $\boldsymbol{p}_\perp^{(0)}(\boldsymbol{m})$ becomes zero, so that $\boldsymbol{m}_0$ is the longitudinal normal of the crystal. But vector fields $\boldsymbol{p}_\perp^{(1,2)}(\boldsymbol{m})$, lying on the internal sheets of the phase velocities surface differ from zero everywhere. It follows that these sheets cannot be separated from each other, since otherwise they would be homeomorphous to a sphere and would have at least one common point. The radius-vector of this point is an acoustic axis. Thus it has been shown that at the given configuration of the phase velocities surface every crystal has at least one acoustic axis*.

The example of paratellurite (TeO_2) shows, however, that other configurations of phase velocities surfaces are also possible. In Fig. 56.14*b* there can be seen the points of contact of the external sheets of this surface; it corresponds to the direction lying in plane (010) and making up an angle of 19.7° with [100]. Fig. 56.15*a* shows that in this direction the beams sharply diverge from the wave normal. Moreover, inside a certain cone surrounding direction [100] which is distant from [100] in plane (010) by 19.7°, and in plane (001) by 8.2°, the external sheet of the phase velocities surface corresponds to the quasitransversal waves, and only the one that follows to the quasilongitudinal waves. This is shown on the graphs of the divergence of the polarization vectors from the wave normal in Fig. 56.15*b*. It can be seen that under the transition of a quasilongitudinal wave into the quasitransversal one (shown by a dashed line) no peculiar phenomena are observed in plane (001).

Let us return to the problem of the existence of acoustic axes in crystals of arbitrary symmetry. According to the theorem on the vanishing of a continuous vector field tangential to a sphere, a sheet of the phase velocities surface can have common points with other sheets only when its certain point corresponds to a purely longitudinal wave (this meaning that some vicinity of this point corresponds to quasilongitudinal vaves). For acoustic axes to be absent in a crystal it is necessary and sufficient for its phase velocities surface to consist of three sheets, none of which has points common with the others. For this in its turn, it is necessary (but not of course sufficient) that each of the sheets includes at least one point corresponding to a purely longitudinal wave. So the topological analysis does not eliminate the possibility of existence of a crystal without a single acoustic axis, but it shows that such a crystal should have at least three longitudinal normals; in this case the longitudi-

* It can be proved in exactly the same way that any crystal has at least one optic axis, the only difference being that the equations of the optic surfaces are simpler and the directions of optic axes can be easily found from them, while a similar investigation of the equations of acoustic surfaces is difficult.

nal wave corresponding to one of the normals must have a greater phase velocity than the transversal waves isonormal to it; the longitudinal wave corresponding to another normal must have a lesser phase velocity, and the wave corresponding to the third normal must have a phase velocity intermediate between those of the transversal waves isonormal to it. It should be emphasized, however, that a direct analysis of the equation of the phase velocities surface (56.25) can give more accurate results (just as F. I. Fedorov's theorem proves the existence of at least two longitudinal normals in any crystal, while from the topological considerations it only follows that at least one longitudinal normal exists).

For further investigation of the velocities surface and other acoustic surface of crystals, we shall return to the determination of the beam velocity (56.9) and shall consider the dependence of ω on the length of the wave vector $\boldsymbol{k} = k\boldsymbol{m}$ and its direction $\boldsymbol{m}$ (beam velocity):

$$w_i = \frac{\partial\omega}{\partial k_i} = \frac{\partial\omega}{\partial k}\frac{\partial k}{\partial k_i} + \frac{\partial\omega}{\partial m_j}\frac{\partial m_j}{\partial k_i}. \tag{56.26}$$

Let us discuss the individual derivatives contained in the expansion (56.26). From relation $\omega = vk$ we find $\partial\omega/\partial k = v$ and $\partial\omega/\partial m_j = k\partial v/\partial m_j$. The other derivatives are equal respectively to

$$\frac{\partial k}{\partial k_i} = \frac{\partial\sqrt{k_i k_i}}{\partial k_i} = \frac{k_i}{k} = m_i,$$

$$\frac{\partial m_j}{\partial k_i} = \frac{\partial(k_j/k)}{\partial k_i} = \frac{1}{k^2}\left(k\frac{\partial k_j}{\partial k_i} - \frac{\partial k}{\partial k_i}k_j\right) = \frac{1}{k}(\delta_{ij} - m_i m_j).$$

Substituting these expressions into (56.26) we have*

$$w_i = vm_i + (\delta_{ij} - m_i m_j)\frac{\partial v}{\partial m_j}, \quad \boldsymbol{w} = v\boldsymbol{m} + (\mathbf{I} - \boldsymbol{m}\boldsymbol{m})\cdot\frac{\partial v}{\partial \boldsymbol{m}}. \tag{56.27}$$

Thus the vector of beam velocity $\boldsymbol{w}$ appears as the sum of the vector of phase velocity $\boldsymbol{v} = v\boldsymbol{m}$ and of that part of the derivative $\partial v/\partial \boldsymbol{m}$ which is perpendicular to the wave normal $\boldsymbol{m}$ (see Sec. 18). This is in full agreement with (56.15).

It follows from formula (56.27) that in those directions to which correspond the stationary points of the velocities surface (where $\partial v/\partial \boldsymbol{m} = 0$, i.e. the radius-vector is normal to the surface) ordinary waves propagate. Formula (56.27) also shows that the beam diverges from the wave normal the greater, the faster the phase velocity v changes with direction, the beam diverging from the normal in the

* The seeming contradiction between formula (56.27) and the one given by F. I. Fedorov (1965, p. 140), $\boldsymbol{w} = d v/\partial \boldsymbol{m}$ is due to the fact that in the latter formula the differentiation with respect to $\boldsymbol{m}$ is performed without account taken of relation $\boldsymbol{m}\cdot\boldsymbol{m} = 1$, while in (56.27) this condition is taken into account.

direction of the velocity increase. Thus the vectors of beam velocities are "concentrated" in those directions in which the corresponding

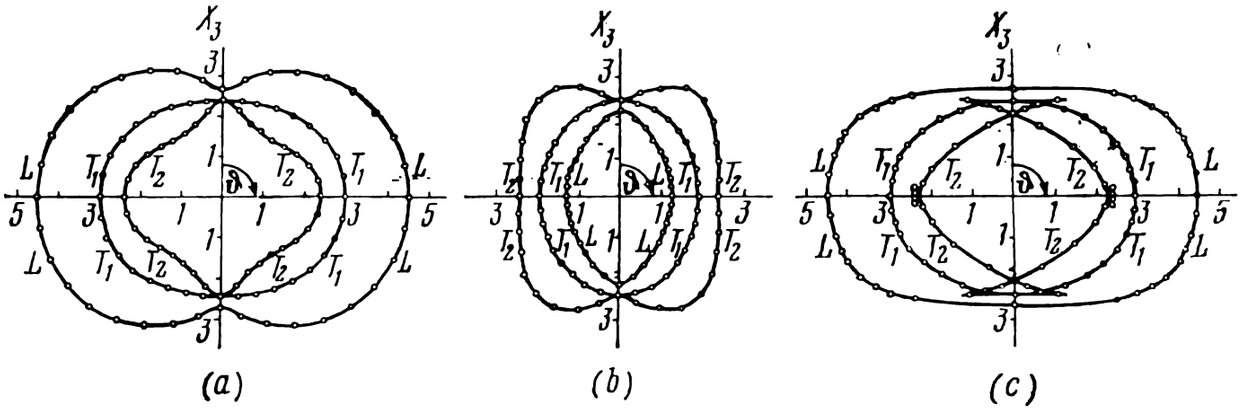


Fig. 56.4. Surfaces of phase velocities (a), reciprocal velocities multiplied by c_{44}/ρ (b) and of beam velocities (c) of a zinc crystal, class $6/mmm$. Sections by a plane passing through the principal symmetry axis; L are the quasilongitudinal waves, T_1 are the transversal waves, T_2 are the quasitransversal waves; in km/s (Musgrave, 1954)

sheets of the velocities surface are most distant from the centre.

Stationary points of the phase velocities surface of zinc (Fig. 56.4*a*) are located not only on the pole and on the equator but also (on the

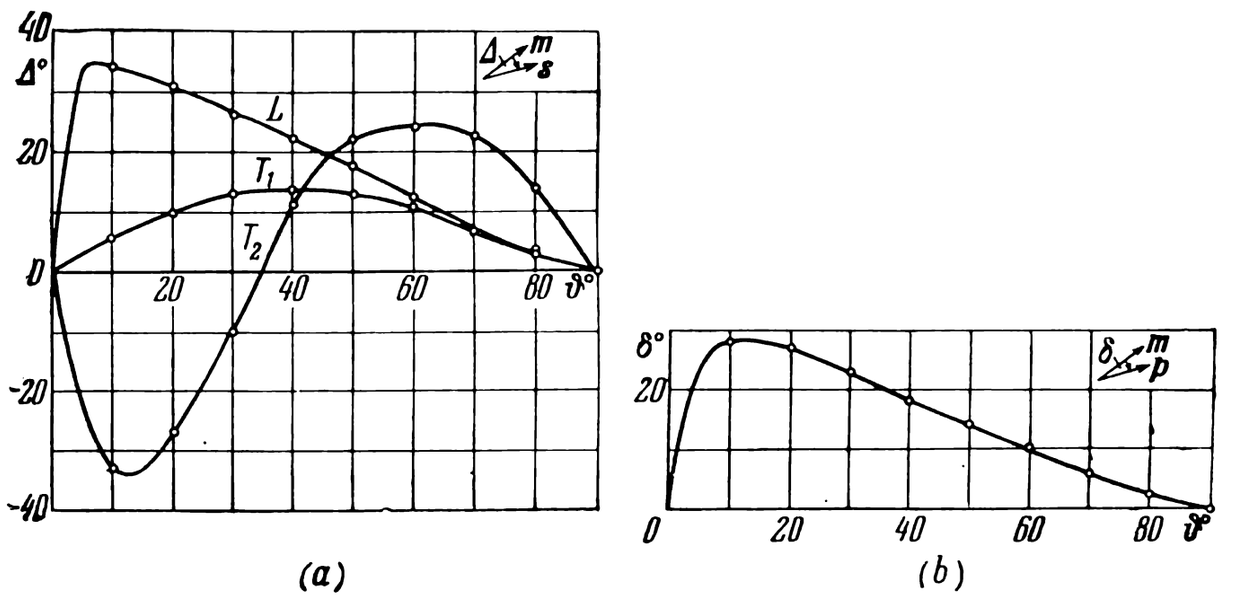


Fig. 56.5. Divergence of beams (a) and of the polarization vector of a quasilongitudinal wave (b) from the wave normal in a zinc crystal. Angle ϑ is plotted from [0001] to (000_{-1}); angles Δ and δ are considered positive with the deflection toward (0001); L, T_1, T_2—see Fig. 56.4 (Musgrave, 1954)

sheet of quasitransversal waves T_2) between them. Fig. 56.5*a* shows that the divergence of a corresponding beam from the wave normal at $\vartheta \approx 37°$ actually becomes zero, so that wave T_2 in this direction

is ordinary. On the phase velocities surface of beryl (Fig. 56.6*a*) the stationary points, besides being on the pole and the equator, are found on the sheet of quasitransversal (T_2) waves and also on the sheet of quasilongitudinal (L) waves, and Fig. 56.7*a* shows that the

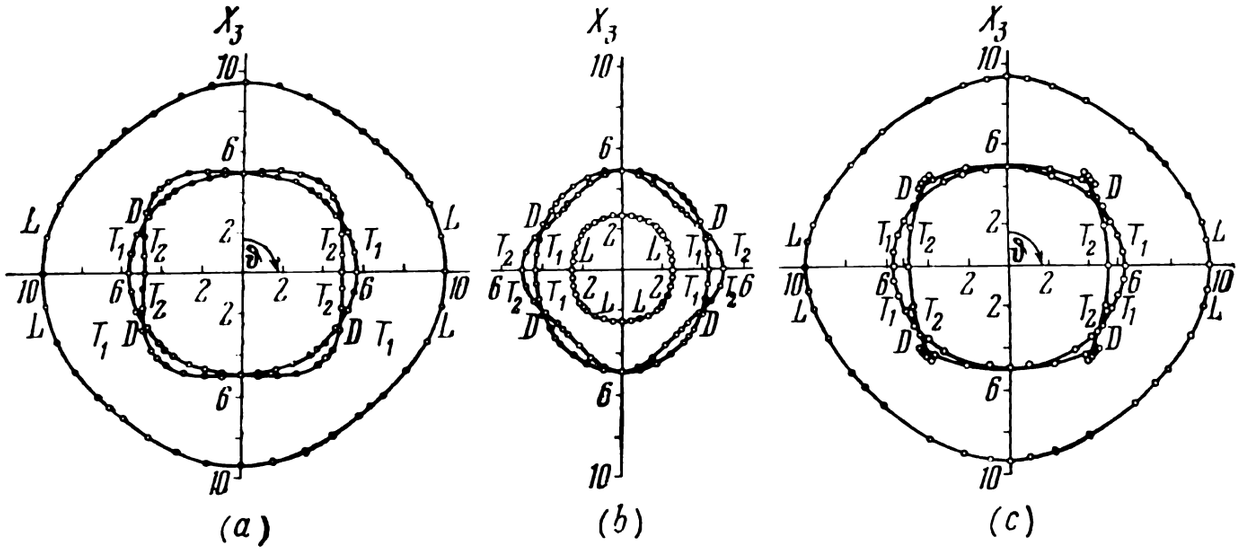


Fig. 56.6. Surfaces of phase velocities (a), reciprocal velocities multiplied by c_{44}/ρ (b) and beam velocities (c) in a beryl crystal, class 6/*mmm*. Sections by a plane passing through the principal symmetry axis; L are the quasilongitudinal waves, T_0 are the transversal waves, T_2 are the quasitransversal waves; in km/s (Musgrave, 1954)

divergences of the beams L and T_2 at the corresponding angles become zero, as it should be. On the other hand, a quasilongitudinal wave becoming purely longitudinal becomes at the same time an

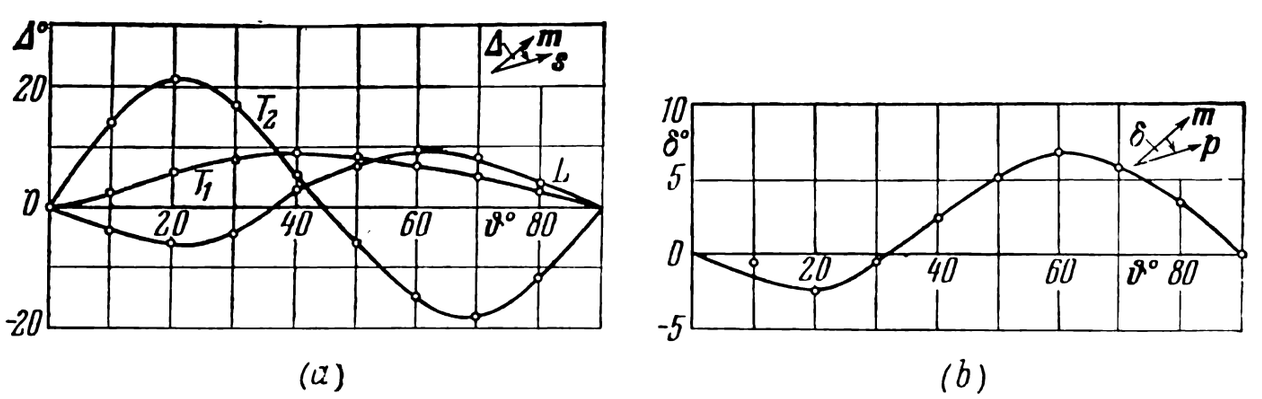


Fig. 56.7. Divergence of beams (a) and of the polarization vector of a quasilongitudinal wave (b) from the wave normal in a beryl crystal. Notation is the same as in Fig. 56.4 (Musgrave, 1954)

ordinary wave, i.e. together with the divergence of the polarization vector from the wave normal the divergence of the beam from the wave normal also becomes zero (the graphs in Fig. 56.7 are probably plotted not accurately enough but in Fig. 56.13 this fact is shown very lucidly).

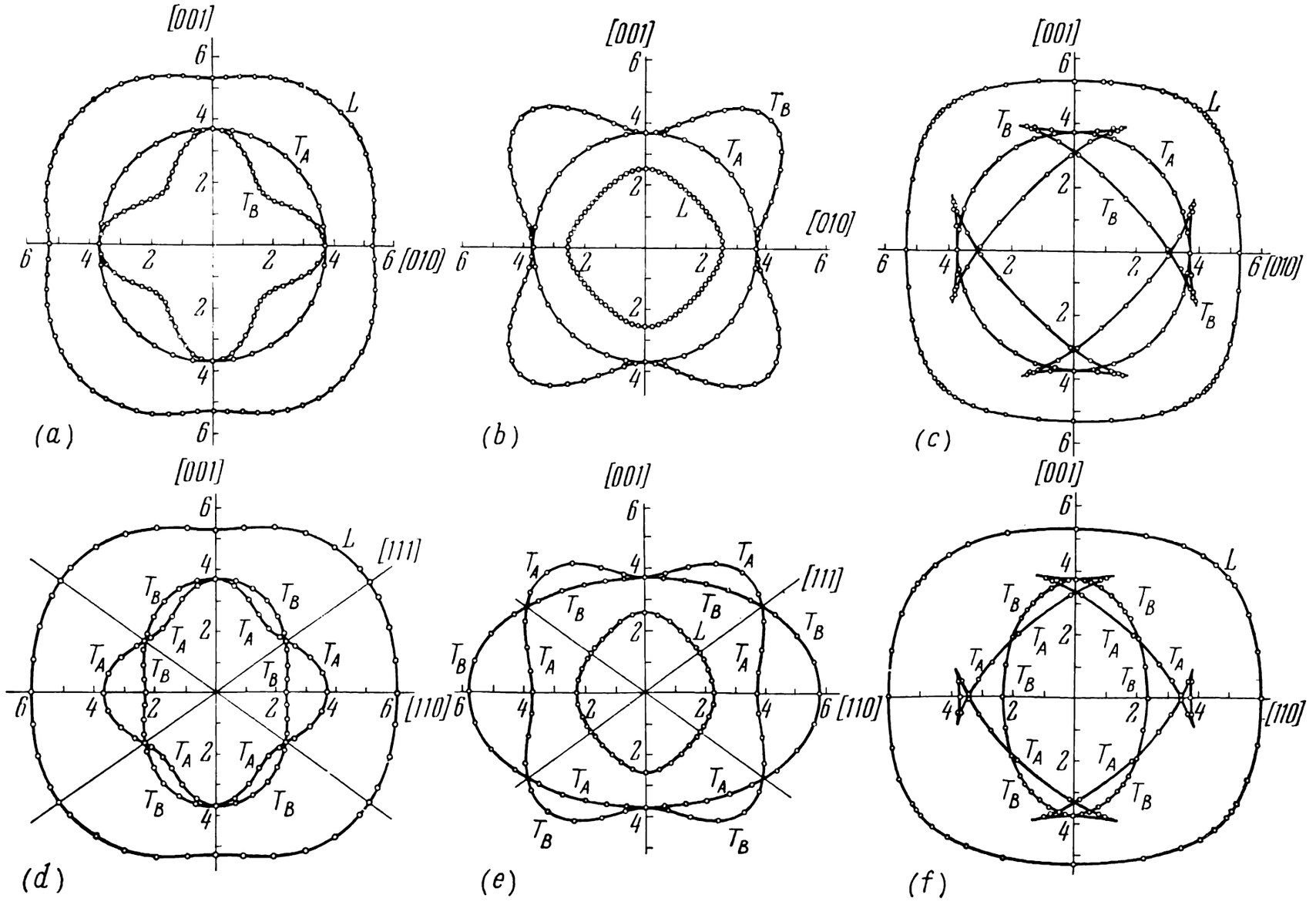


Fig. 56.8. Surfaces of phase velocities (a and d), or reciprocal velocities multiplied by c_{44}/ρ (b and e) and of beam velocities (c and f) of a nickel crystal, class $m3m$; a, b, c are the sections by plane (100), d, e, f are the sections by plane (110); L are the longitudinal waves, T_A are the transversal waves, T_B are the quasitransversal waves; in km/s (Miller, Musgrave, 1956)

On the sections of the phase velocities surfaces of cubic crystals by planes {001}, see Figs. 56.8*a* and 56.9*a*, circumferences character-

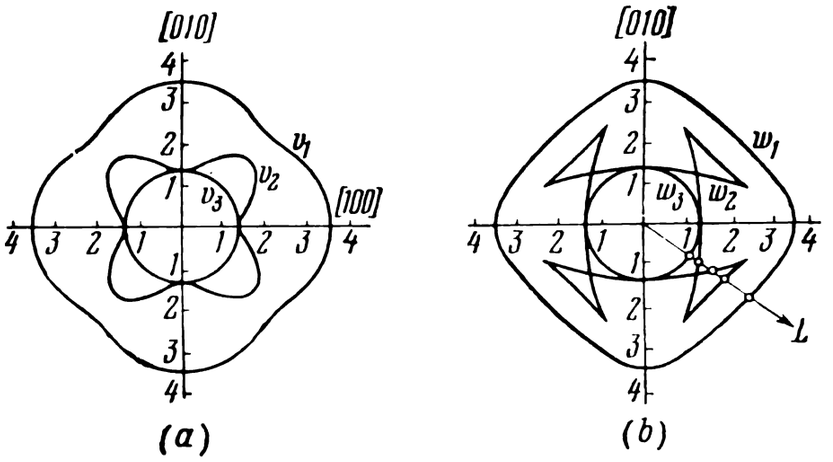


Fig. 56.9. Sections of the surface of phase velocities (a) and beam velocities (b) of a KBr crystal, class $m3m$, by plane (001). L is the direction of the beam to which five waves with different normals correspond (see Fig. 56.10); in km/s (K. S. Alexandrov, 1958)

ize the plane {001} as being an isotropic plane for the transversal waves polarized perpendicular to it. The stationary points on the sections of the phase velocities surfaces by planes {001} (Figs. 56.8*a* and 56.9*a*) and $\{1\bar{1}0\}$ (Fig. 56.8*d*) correspond to ordinary waves. The Figures show that in directions ⟨001⟩ and ⟨110⟩ all waves are ordinary, as it should be, while in directions ⟨111⟩ only longitudinal waves are ordinary. On section $\{1\bar{1}0\}$ we can see the directions not specified by the crystal symmetry in which ordinary waves also propagate (transversal ones, $\boldsymbol{p} \parallel \langle 110 \rangle$). The comparison of Figs. 56.8*a* and 56.9*a* shows the effect of the anisotropy sign (see Sec. 52) on the character of the velocities surface: for a nickel crystal the coefficient $C_N^{\{4\}} = (2/5)\ (c_{11} - c_{12} - 2c_{44}) < 0$ and correspondingly $A = 2c_{44}/(c_{11} - c_{12}) > 1$, for a crystal of KBr $C_N^{\{4\}} > 0$ and $A < 1$. At $C_N^{\{4\}} > 0$ the velocity of longitudinal waves is at its maximum in the directions ⟨100⟩ and at its minimum in the directions ⟨111⟩, while at $C_N < 0$ the situation is opposite; other similar regularities can also be easily noticed. Figs. 56.11 and 56.12

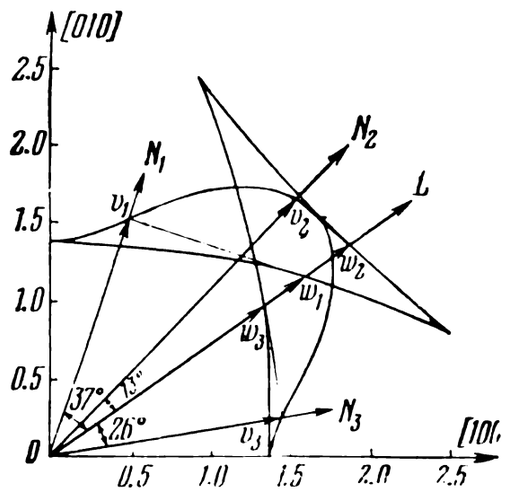


Fig. 56.10. Sections of the surfaces of phase and beam velocities for quasitransversal waves propagating and polarized in plane (001) for a KBr crystal. L is the direction of the beam, w_1, w_2, w_3 are the beam velocities of three such waves propagating along the beam L; v_1, v_2, v_3 are their phase (normal) velocities; N_1, N_2, N_3 are the directions of the wave normals; in km/s (K. S. Alexandrov, 1958)

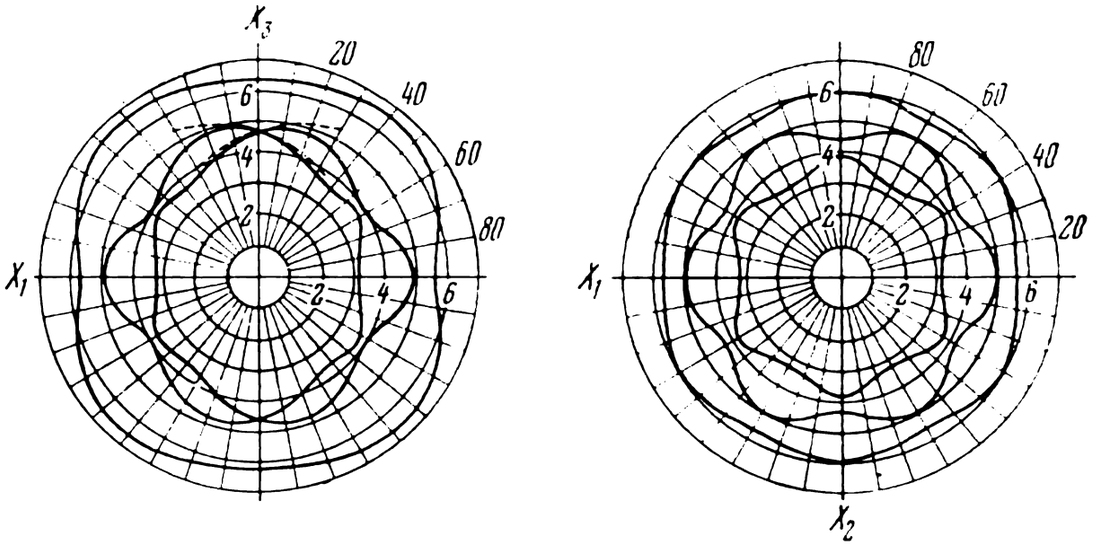


Fig. 56.11. Sections of the surface of phase velocities of elastic waves in a quartz crystal class 32, by coordinate planes; in km/s (Farnell, 1961)

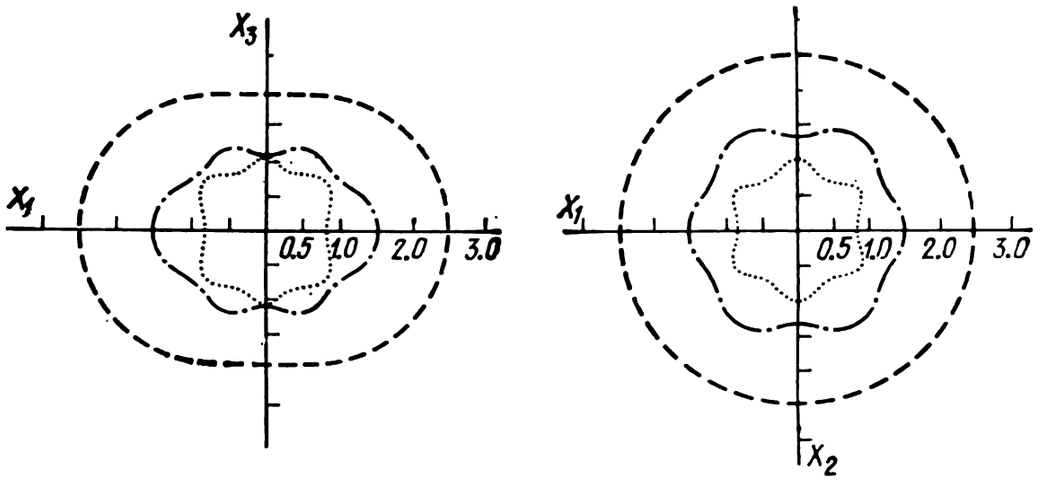


Fig. 56.12. Sections of the s rface of phase velocities of elastic waves in a bismuth crystal, class $\bar{3}m$, by coordinate planes of a crystal-physical system. Dashed lines correspond to quasilongitudinal waves, dotted and dashed-dotted lines correspond to quasitransversal waves. A is the direction of a longitudinal normal; in km/s (Pace, Saunders, 1971)

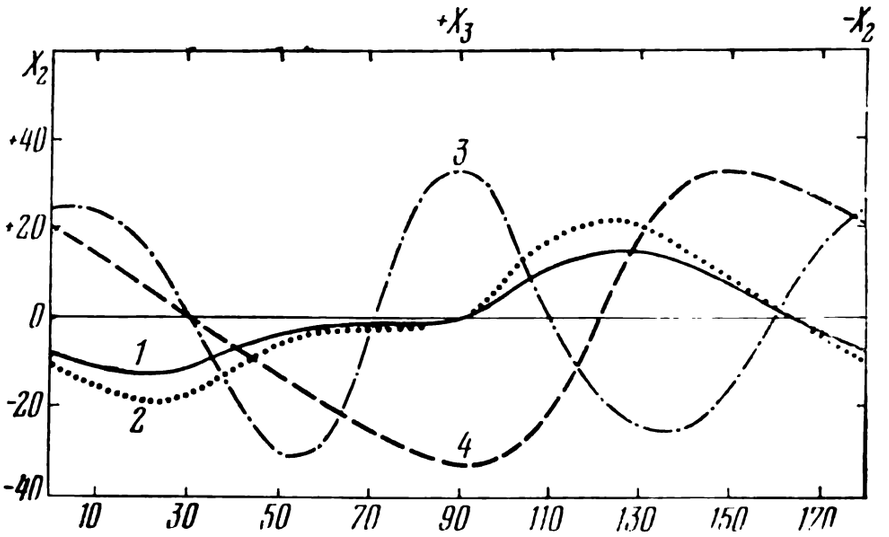


Fig. 56.13. Deviation (in degrees) of the polarization vector of a quasilongitudinal wave (1) and beam vectors of a quasilongitudinal (2) and quasitransversal (3 and 4) waves from the vector of the wave normal for waves propagating in the symmetry plane X_3X_2 (cf. Fig. 56.12) of a bismuth crystal (Pace, Saunders, 1971)

show the sections of the phase velocities surfaces of two trigonal crystals by the coordinate planes, and Fig. 56.14 shows the same for a tetragonal crystal. Fig. 56.13 shows the divergences of the polarization of quasilongitudinal waves and of beam velocity from a wave normal. The latter are shown also in Fig. 56.15; they reach 73° (see Fig. 56.15*b*).

Along with a phase velocities surface *refraction surfaces* (F. I. Fedorov, 1965) are also used; they are also called *reciprocal velocities surfaces* or *slouwness surfaces*. They are locuses of the ends of all possible refraction vectors $\boldsymbol{n} = \boldsymbol{m}/v$ plotted from one point. The equation of the surface

$$\det \| c_{ijkl} n_j n_k - \rho \delta_{il} \| = 0, \quad (56.28)$$

as well as (56.25) is derived from the condition of the existence of non-zero solutions of Christoffel equations, but in distinction from (56.25) it is an equation of sixth degree. In every direction the radius-vectors of the refraction surface and phase velocities surface are mutually reciprocal: $n(\boldsymbol{m}) = 1/v(\boldsymbol{m})$; therefore when we know the form of one of the surfaces, we can easily imagine that of the other. Three such surfaces are shown in Figs. 56.4*b*, 56.6*b*, 56.8*b*. The are analogous to the refractive indices surfaces used in crystal optics.

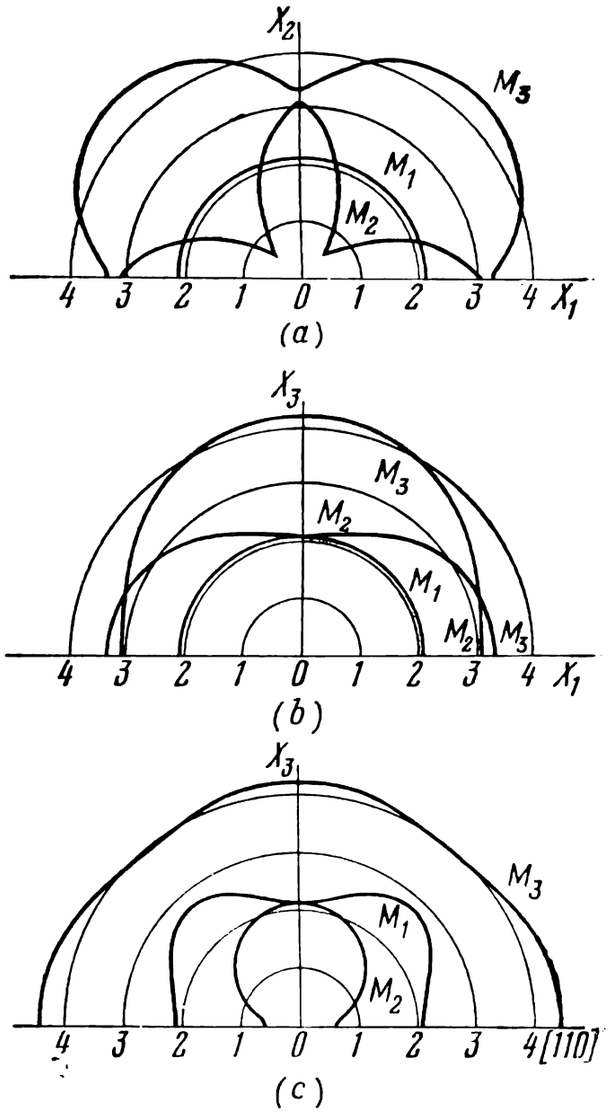


Fig. 56.14. Sections of the surface of phase velocities of ealstic waves in a paratellurite, TeO_2, crystal, class 422:
(a) by plane (001); (b) by plane (0.10); (c) by plane (110); in km/s (Ohmachi, Uchida, Niizeki, 1972)

If from some point O all the possible vectors of beam velocity $\boldsymbol{w}$ are marked off, their ends will form the *beam velocities surface*. It is also called the *wave surface*, since it represents, as it follows from its definition, the locus of points simultaneously reached by an acoustic wave emitted from a point source located at O. Therefore a normal to the wave surface is a wave normal, and a plane tangential to it is a wave-front plane. A perpendicular dropped from point O onto the tangential plane is a phase velocity vector $\boldsymbol{v}$. If tangential planes

are constructed in each point of the wave surface, the ends of the perpendiculars dropped onto them from the centre of the wave surface will form a velocities surface; this means that the latter is the pedal curve of the wave surface. In the directions in which ordinary waves propagate, the corresponding sheets of the wave surface and the velocities surfaces come in contact and a radius-vector serves as their common normal. The relation between the surfaces of the phase and beam velocities is shown in Fig. 56.10.

In crystal acoustics there are no duality relations that are so characteristic of crystal optics (see Sec. 36)*. This is evident, in

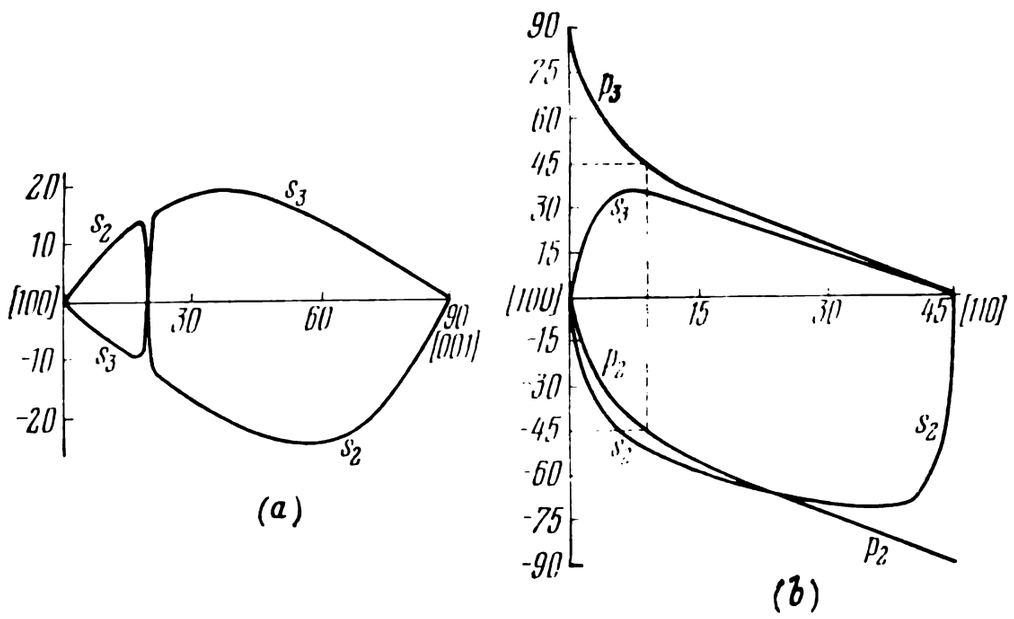


Fig. 56.15. Deviation in degrees of the polarization vector p and beam s from the wave normal in paratellurite: (a) in plane (001), (b) in plane $(1\bar{1}0)$. Indices correspond to those in Fig. 56.14. After Ohmachi, Uchida, Niizeki (1972).

particular, from the fact that the equation of the beam velocities surface is much more complicated than the equations of the phase velocities (56.25) and refraction (56.28) surfaces: its degree, and consequently the order of the surface can attain 150 (F. I. Fedorov, 1965). The surface itself is correspondingly also more complicated. As distinct from a velocities surface, it can have, besides points and lines of self-intersection (exits of acoustic axes), breaks (lines of return). So far only sections of these surfaces by symmetry planes have been investigated (F. I. Fedorov, 1965). For hexagonal crystals they are shown in Figs. 56.4*c* and 56.6*c*.

The sections of beam velocities surfaces of cubic crystals by planes {100} and {110} are shown in Figs. 56.8*c* and *f* and 56.9*b*. Let us

* For general information on the analogy between crystal acoustics and crystal optics see K. S. Alexandrov (1956, 1975) and Henneke and Green (1969).

compare them with the sections of the phase velocities surfaces. Plane {001} sections the sheet corresponding to the purely transversal waves in this plane, along a circumference which coincides with the section of the phase velocities surface, while the section of the sheet by plane {110} is an ellipse whose semi-axes are equal to the semi-axes of the phase velocities oval. The shapes of the sections of the sheet corresponding to waves that are quasishear in the {100} and {110} planes are very complicated because of breaks. Thus, in cubic crystals (as well as in hexagonal ones, see Figs. 56.4*c* and 56.6*c*) there can exist directions along which not three but five elastic waves of different velocities can propagate: a quasilongitudinal wave, a transversal one and three quasitransversal ones, i.e. five normals correspond to a single beam, although just three beams i.e. three directions of the propagation of energy always correspond to one normal. This phenomenon was examined in detail (see Fig. 56.10) and experimentally verified by K. S. Alexandrov (1958) in a KBr crystal.

On the theory of elasticity of crystals and on the associated problems see Alexandrov (1962, 1975); Goldenblat (1969); Ilyushin (1971); Koptsik, Sirotin (1961); Landau and Lifshits (1965); Lekhnitsky (1959); Lurie (1955, 1970); Sedov (1962 and 1970); F. I. Fedorov (1965); Leibfried (1961); Love (1944); Auld (1973); Dieulesaint, Royer (1974); Musgrave (1970).

Chapter VII

THERMODYNAMICS OF CRYSTALS

Sec. 57. Internal Energy and Thermodynamic Potential of a Crystal

The work done over a crystal unit volume by an electric field and mechanical stresses equals respectively

$$\delta R_{\text{el}} = \frac{1}{4\pi} E_i \, dD_i = \frac{1}{4\pi} \boldsymbol{E} \cdot \boldsymbol{D},$$
$$\delta R_{\text{mech}} = \sigma_{ij} \, d\varepsilon_{ij} = \sigma_\lambda \sigma \varepsilon_\lambda = \sigma : d\varepsilon. \tag{57.1}$$

If we introduce vector $\widetilde{\boldsymbol{D}} = \boldsymbol{D}/4\pi$ for the uniformity of formulas, then the general change of the internal energy in the unit of crystal volume under infinitesimal thermal, mechanical and electrical forces can be written as follows

$$dU = T \, dS + E_i d\widetilde{D}_i + \sigma_\lambda d\varepsilon_\lambda \tag{57.2}$$

(T is the absolute temperature, S is the entropy per unit volume).

Expression (57.2) is incorrect from a strictly formal point of view. The fact is that a solid body the stresses in which do not reduce to uniform extension is not in the state of thermodynamic equilibrium. Actually it can recrystallize with time so that its shape remains unchanged, but all the stresses, except the uniform extension, will vanish, and then will full thermodynamic equilibrium be attained. Since too much time is required for setting the equilibrium, we often have to deal with solids in which the equilibrium has not been reached yet. Such solids are described by expression (57.2).

Entropy, electric induction, strain components are usually called the *generalized thermodynamic coordinates*, while temperature, electric field strength, mechanical stresses are called the *generalized thermodynamic forces*.

We introduce the following notation for them:

S	$\widetilde{D}_1$	$\widetilde{D}_2$	$\widetilde{D}_3$	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6
x_0	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9
T	E_1	E_2	E_3	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
X_0	X_1	X_2	X_3	X_4	X_5	X_6'	X_7	X_8	X_9

In this notation the total differential of internal energy (57.2) takes the form

$$dU = X_A dx_A \tag{57.3}$$

(here and later indices A, B, C run through 0, 1, . . ., 9).

The quantities X_A and x_A can be regarded as the components of vectors in a 10-dimensional space; then the product $X_A dx_A$ takes the meaning of a scalar product.

Formula (57.3) allows calling the internal energy the thermodynamic potential with respect to the generalized coordinates, because any generalized force is equal to the derivative of the internal energy with respect to a corresponding generalized coordinate

$$X_A = \frac{\partial U}{\partial x_A}, \tag{57.4}$$

when the other generalized coordinates are considered to be constant, i.e. the internal energy is regarded as a function of the generalized coordinates and not of any other variables. It is more convenient, however, to use generalized forces, and not generalized coordinates, as independent variables: in conducting an experiment we usually can adjust and measure temperature, electric field strength, mechanical stresses, while direct adjustment of the entropy, electric induction and strains is cumbersome.

The role of the thermodynamic potential vith respect to the generalized forces is played by the function

$$\Phi = U - TS - E_i\tilde{D}_i - \sigma_\lambda \varepsilon_\lambda = U - X_A x_A, \tag{57.5}$$

the total differential of which is

$$d\Phi = -S\,dT - \tilde{D}_i dE_i - \varepsilon_\lambda\, d\sigma_\lambda = -x_A\, dX_A; \tag{57.6}$$

it is called the *thermodynamic potential* (in the narrow sense of the word) of the *Gibbs free energy*. If it is regarded as a function of generalized forces, then any generalized coordinate equals

$$x_A = -\frac{\partial \Phi}{\partial X_A}. \tag{57.7}$$

Les us expand this expression into a Taylor series in the vicinity of an arbitrary point $X_B = X_B^{(0)}$, i.e. of an arbitrary initial state of the crystal characterized by fixed values of $X_B^{(0)}$ of the generalized thermodynamic forces, and confine ourselves to the first-order terms:

$$x_A = -\frac{\partial \Phi}{\partial X_A} = -\left(\frac{\partial \Phi}{\partial X_A}\right)_0 - \left(\frac{\partial^2 \Phi}{\partial X_A\, \partial X_B}\right)_0 (X_B - X_B^{(0)}) - \ldots \tag{57.8}$$

Here $(\partial\Phi/\partial X_A)_0 = x_A^{(0)}$ is the value of the corresponding generalized thermodynamic coordinate of the crystal in its initial state, when all generalized thermodynamic forces are equal to $X_B^{(0)}$, and $(\partial^2\Phi/\partial X_A \partial X_B)_0$ is the value of its derivative under the same conditions.

An unstressed (all $\sigma_\lambda = 0$) state of the crystal in the absence of electric field (all $E_i = 0$) can conveniently be chosen as the initial state. Thus only $X_0^{(0)} = T_0$, i.e. the initial temperature of the crys-

tal from among the initial values of the generalized thermodynamic forces, is non-zero. Let us agree that the crystal in its initial state is neither strained nor polarized; this simply means that the temperature T_0 is taken as the point of reference for temperature deformations and pyroelectric polarization*. Let us denote the deviations of temperature and entropy from their initial values $T - T_0 = \Theta$, $S - S_0 = \Sigma$ and introduce, along with x_A and X_A,

$$y_A = \begin{cases} \Sigma & \text{at } A=0, \\ x_A & \text{at } A=1, \ldots, 9; \end{cases} \qquad Y_A = \begin{cases} \Theta & \text{at } A=0, \\ X_A & \text{at } A=1, \ldots, 9. \end{cases}$$

The expansions (57.8) can now be written as

$$y_A = -\left(\frac{\partial^2\Phi}{\partial Y_A\,\partial Y_B}\right)_0 Y_B = M_{AB}Y_B, \tag{57.9}$$

$M_{AB} = -(\partial^2\Phi/\partial Y_A\partial Y_B)_0 = -(d^2\Phi/\partial X_A\partial X_B)_0$ being the values of the corresponding derivatives, when all $Y_B = 0$.

The set of numbers M_{AB} can be regarded as a matrix of a tenth order that transforms a set of ten-dimensional vectors of the generalized forces Y_A into a set of also ten-dimensional vectors of the generalized coordinates y_A. This matrix is called the *matrix of the thermodynamic potential* Φ; being composed of its second derivatives it is obviously symmetric:

$$M_{AB} = M_{BA}. \tag{57.10}$$

Expansion (57.9) can be written in a fuller form as follows:

$$\begin{aligned} \Sigma &= -\left(\frac{\partial^2\Phi}{\partial T^2}\right)_0 \Theta - \left(\frac{\partial^2\Phi}{\partial T\,\partial E_k}\right)_0 E_k - \left(\frac{\partial^2\Phi}{\partial T\,\partial\sigma_\mu}\right)_0 \sigma_\mu, \\ \tilde{D}_i &= -\left(\frac{\partial^2\Phi}{\partial E_i\,\partial T}\right)_0 \Theta - \left(\frac{\partial^2\Phi}{\partial E_i\,\partial E_k}\right)_0 E_k - \left(\frac{\partial^2\Phi}{\partial E_i\,\partial\sigma_\mu}\right)_0 \sigma_\mu, \\ \varepsilon_\lambda &= -\left(\frac{\partial^2\Phi}{\partial\sigma_\lambda\,\partial T}\right)_0 \Theta - \left(\frac{\partial^2\Phi}{\partial\sigma_\lambda\,\partial E_k}\right)_0 E_k - \left(\frac{\partial^2\Phi}{\partial\sigma_\lambda\,\partial\sigma_\mu}\right)_0 \sigma_\mu. \end{aligned} \tag{57.11}$$

To reveal the physical meaning of the derivative $(\partial^2\Phi/\partial T^2)_0$ we compute the change of the entropy of the unit of crystal unit volume with the rise of temperature by Θ in the absence of electric field and mechanical stresses: $\Sigma = -(\partial^2\Phi/\partial T^2)_0\Theta$. In this case the crystal unit volume receives

$$Q = C_p\Theta,$$

of heat where C_p is the heat capacity of the crystal per unit volume with constant electric field and constant mechanical stresses. On the other hand, since $\Theta/T \ll 1$ (otherwise the expansions could not be

* Spontaneous polarization is not considered here; for ordinary pyroelectrics—for the reasons given in Sec. 31, for ferroelectrics—because the approximation used here is not sufficient for them.

confined to the first term for temperature, this heat approximately equals

$$Q = T_0\Sigma.$$

Comparing these expressions, we find

$$-\left(\frac{\partial^2\Phi}{\partial T^2}\right)_0 = \frac{C_p}{T_0}. \tag{57.12}$$

The other elements of the matrix of the thermodynamic potential have the following names and notation: dielectric permittivity coefficients (divided by 4π)

$$\tilde{\varkappa}_{ik} = \frac{1}{4\pi}\varkappa_{ik} = -\left(\frac{\partial^2\Phi}{\partial E_i\,\partial E_k}\right)_0, \quad \frac{1}{4\pi}\boldsymbol{\varkappa} = -\left(\frac{\partial^2\Phi}{\partial \mathbf{E}\,\partial \mathbf{E}}\right)_0; \tag{57.13}$$

elastic compliance coefficients

$$s_{\lambda\mu} = -\left(\frac{\partial^2\Phi}{\partial\sigma_\lambda\,\partial\sigma_\mu}\right)_0, \quad \mathbf{s} = -\left(\frac{\partial^2\Phi}{\partial\boldsymbol{\sigma}\,\partial\boldsymbol{\sigma}}\right)_0; \tag{57.14}$$

pyroelectric coefficients

$$p_i = -\left(\frac{\partial^2\Phi}{\partial E_i\,\partial T}\right)_0, \quad \mathbf{p} = -\left(\frac{\partial^2\Phi}{\partial \mathbf{E}\,\partial T}\right)_0; \tag{57.15}$$

thermal expansion coefficients

$$\alpha_\lambda = -\left(\frac{\partial^2\Phi}{\partial\sigma_\lambda\,\partial T}\right)_0, \quad \boldsymbol{\alpha} = -\left(\frac{\partial^2\Phi}{\partial\boldsymbol{\sigma}\,\partial T}\right)_0 \tag{57.16}$$

and finally, piezoelectric coefficients

$$d_{i\mu} = -\left(\frac{\partial^2\Phi}{\partial E_i\,\partial\sigma_\mu}\right)_0, \quad \mathbf{d} = -\left(\frac{\partial^2\Phi}{\partial\mathbf{E}\,\partial\boldsymbol{\sigma}}\right)_0. \tag{57.17}$$

All these coefficients, except the piezoelectric ones which will be considered in Sec. 58, have been already discussed in the preceding chapters.

The thermodynamic potential matrix M is expressed in terms of these coefficients as follows:

$$M = \begin{Vmatrix} C_p/T_0 & p_1 & p_2 & p_3 & \alpha_1 & \alpha_2 & \alpha_3 & \alpha_4 & \alpha_5 & \alpha_6 \\ p_1 & \tilde{\varkappa}_{11} & \tilde{\varkappa}_{12} & \tilde{\varkappa}_{31} & d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ p_2 & \tilde{\varkappa}_{12} & \tilde{\varkappa}_{22} & \tilde{\varkappa}_{23} & d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ p_3 & \tilde{\varkappa}_{31} & \tilde{\varkappa}_{23} & \tilde{\varkappa}_{33} & d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \\ \alpha_1 & d_{11} & d_{21} & d_{31} & s_{11} & s_{12} & s_{31} & s_{14} & s_{15} & s_{16} \\ \alpha_2 & d_{12} & d_{22} & d_{32} & s_{12} & s_{22} & s_{23} & s_{24} & s_{25} & s_{26} \\ \alpha_3 & d_{13} & d_{23} & d_{33} & s_{31} & s_{23} & s_{33} & s_{34} & s_{35} & s_{36} \\ \alpha_4 & d_{14} & d_{24} & d_{34} & s_{14} & s_{24} & s_{34} & s_{44} & s_{45} & s_{64} \\ \alpha_5 & d_{15} & d_{25} & d_{35} & s_{15} & s_{25} & s_{35} & s_{45} & s_{55} & s_{56} \\ \alpha_6 & d_{16} & d_{26} & d_{36} & s_{16} & s_{26} & s_{36} & s_{64} & s_{56} & s_{66} \end{Vmatrix}.$$

Now formulas (57.11) are finally written out as:

$$\Sigma = (C_p/T_0)\,\Theta + p_k E_k + \alpha_\mu \sigma_\mu, \tag{57.18a}$$

$$\widetilde{D}_i = p_i \Theta + \widetilde{\varkappa}_{ik} E_k + d_{i\mu} \sigma_\mu, \tag{57.18b}$$

$$\varepsilon_\lambda = \alpha_\lambda \Theta + d_{k\lambda} E_k + s_{\lambda\mu} \sigma_\mu, \tag{57.18c}$$

or in a non-coordinate form

$$\boldsymbol{\Sigma} = (C_p/T_0)\,\Theta + \boldsymbol{p}\cdot\boldsymbol{E} + \boldsymbol{\alpha} : \boldsymbol{\sigma}, \tag{57.18a'}$$

$$\boldsymbol{D} = \boldsymbol{p}\Theta + \widetilde{\boldsymbol{\varkappa}}\cdot\boldsymbol{E} + \mathbf{d} : \boldsymbol{\sigma}, \tag{57.18b'}$$

$$\boldsymbol{\varepsilon} = \boldsymbol{\alpha}\Theta + \boldsymbol{E}\cdot\mathbf{d} + \boldsymbol{s} : \boldsymbol{\sigma}. \tag{57.18c'}$$

At $\boldsymbol{\sigma} = 0$ formula (57.18b) becomes a material equation of electrostatics*, while formula (57.18c) at $\boldsymbol{E} = 0$ becomes Hooke's law with temperature terms. The symmetry of the thermodynamic potential matrix is thus followed by the symmetry of the dielectric permittivity tensor

$$\varkappa_{ik} = \varkappa_{ki} \tag{57.19}$$

and of the elastic compliance coefficients

$$s_{\lambda\mu} = s_{\mu\lambda}, \quad s_{ijkl} = s_{klij}. \tag{57.20}$$

When written out in full, at $\boldsymbol{E} \neq 0$, $\boldsymbol{\sigma} \neq 0$, formulas (57.18b) and (57.18c) point to the possible dependence of electric induction on mechanical stresses and of the strain tensor on the electric field strength, both relations being defined by the same set of coefficients $d_{i\mu}$. The piezoelectric and the converse piezoelectric effects, described in Sec. 58, are connected with them respectively.

Formula (57.18*a*) shows that the entropy of a crystal can depend not only on temperature but also on the electric field and mechanical stresses. If follows from the symmetry of matrix M that the corresponding dependence is defined by the pyroelectric coefficients and thermal expansion coefficients respectively. Thus under the action of electric field $\boldsymbol{E}$ the entropy of unit volume of a pyroelectric crystal changes by

$$\Sigma = p_k E_k = \boldsymbol{p}\cdot\boldsymbol{E}. \tag{57.21}$$

Consequently, a crystal unit volume absorbs heat from its surroundings

$$Q = T_0 \Sigma = T_0 \boldsymbol{p}\cdot\boldsymbol{E}. \tag{57.22}$$

* There is no term $\widetilde{D}^{(0)} = P^{(0)}$ here that characterizes the spontaneous polarization of pyroelectric crystals. We have already seen in Ch. III that the influence of spontaneous polarization is practically fully neutralized because of the finite conductivity of the crystal, on the one hand, and the settling of ions from the air on the charged surfaces of the crystal, on the other hand. Therefore this term is of no practical importance. The pyroelectric effect, however, is included in the consideration.

The word "absorbs" is used here conventionally. If the angle between vectors $\boldsymbol{p}$ and $\boldsymbol{E}$ is less than 90°, heat is actually absorbed, while in the opposite case it is transmitted from the crystal into the environment. This phenomenon is called the *electrocaloric effect.*

The electrocaloric effect can be observed under other conditions. Let there be no mechanical stresses, as before, but heat exchange with the environment is eliminated. It is naturally to be expected that under these conditions the temperature of a crystal introduced into an electric field would change. And in fact, formula (57.18a) in this case takes the form $0 = (C_p/T_0)\,\Theta + \boldsymbol{p}\cdot\boldsymbol{E}$, since the condition of thermal insulation for a reversible process results in $\Sigma = 0$. Hence the change of temperature

$$\Theta = -(T_0/C_p)\,\boldsymbol{p}\cdot\boldsymbol{E}. \tag{57.23}$$

If the electric field is directed along the pyroelectric coefficients vector, the crystal in the electric field is cooled, in the opposite case it is heated. This fully corresponds of course to the behaviour of a crystal in isothermal conditions.

Let us continue the examination of equality (57.18a). In the absence of an electric field (or with a non-pyroelectric crystal chosen for the experiment) let us subject the crystal to mechanical stresses $\boldsymbol{\sigma}$. If the process goes on isothermally, the crystal absorbs heat

$$Q = T_0\alpha_\mu\sigma_\mu = T_0\boldsymbol{\alpha}:\boldsymbol{\sigma}. \tag{57.24}$$

Heat is actually absorbed if the stresses have the same directions as thermal strains; but in the opposite case heat is liberated. Under the conditions of thermal insulation the temperature change of the crystal subjected to mechanical stresses equals

$$\Theta = -(T_0/C_p)\,\alpha_\mu\sigma_\mu = -(T_0/C_p)\,\boldsymbol{\alpha}:\boldsymbol{\sigma}. \tag{57.25}$$

If the stresses have the same direction with the thermal strains, the crystal is cooled, in the opposite case it is heated. Such phenomena are called the *piezocaloric effect.*

In the majority of crystals all their linear dimensions increase with the rise of temperature: $\boldsymbol{n}\cdot\boldsymbol{\alpha}\cdot\boldsymbol{n} > 0$ ($\boldsymbol{n}$ is a unit vector). Then any tensile stress $\boldsymbol{\sigma} = \sigma\boldsymbol{nn}$ results in the cooling of a thermally insulated crystal, while compression stress leads to its heating. But a crystal of calcite, whose linear dimensions in the basal plane diminish on heating (see Fig. 24.3), is heated under the action of tensile stresses in the basal plane and is cooled under compression stresses. However, the tensile and compression stresses directed along its principal symmetry axis lead to the opposite results.

Sec. 58. Piezoelectric Effect and Its Symmetry

In examining the internal energy and thermodynamic potential of a crystal (Sec. 57) it became evident that the electric polarization of a crystal under the action of mechanical stresses and the strain of a crystal under the action of the electric field are possible. If we leave in formulas (57.18b), (57.18c) only the terms specifying these phenomena, we obtain

$$D_i = 4\pi d_{i\mu}\sigma_\mu, \quad \varepsilon_\lambda = d_{k\lambda}E_k. \tag{58.1}$$

The first of the above formulas describes the piezoelectric effect, the second one—the converse piezoelectric effect. Both effects are characterized by the same set of $d_{i\mu}$ coefficients related to the piezoelectric coefficients tensor

$$\mathbf{d} = \left(\frac{\partial^2\Phi}{\partial E\,\partial\sigma}\right)_0, \quad d_{ikl} = \left(\frac{\partial^2\Phi}{\partial E_i\,\partial\sigma_{kl}}\right)_0 \tag{58.2}$$

by relation (see Appendix F)

$$d_{i\mu} = \begin{cases} d_{ikl} & (kl \leftrightarrow \mu = 1,\ 2,\ 3) \\ 2d_{ikl} & (kl \leftrightarrow \mu = 4,\ 5,\ 6). \end{cases} \tag{58.3}$$

Formulas (58.1) can also be written as follows

$$\begin{aligned} D_i &= 4\pi d_{ikl}\sigma_{kl}, & \boldsymbol{D} &= 4\pi\mathbf{d}:\sigma; \\ \varepsilon_{ij} &= d_{kij}E_k, & \varepsilon &= \boldsymbol{E}\cdot\mathbf{d}. \end{aligned} \tag{58.4}$$

When formulas (58.1) and (58.4) are used, attention should be paid to the role of some indices. In (58.1) the Latin index in $d_{i\mu}$ corresponds to electric quantities and is always in the first place; the Greek index corresponds to mechanical quantities. In (58.4) the first index corresponds to electric quantities, the second and third ones to mechanical quantities. The order of multiplication in (58.4) is in accordance with this.

The piezoelectric coefficients tensor **d** is a third-rank tensor; its internal symmetry is $V\,[V^2]$. It identically equals zero for all centrosymmetric crystals, as well as all matter tensors of the odd type. Thus no piezoelectric effect is possible in centrosymmetric crystals (and generally in the centrosymmetric homogeneous media irrespective of their structure). The form of tensor **d** in non-centrosymmetric groups can be defined with the aid of the methods described in Chapter V. The results of such an investigation are given in Table E.11. It can be seen from the Table that tensor **d** becomes zero in two non-centrosymmetric point groups: in the crystallographic group 432 and in the limit group $\infty\infty$*. In the other 20 crystal-

* This follows from the internal symmetry $V\,[V^2]$ of tensor **d**. A general third-rank tensor, i.e. that with internal symmetry V^3, does not become zero in these groups.

lographic and 3 limit classes the piezoelectric effect is possible. In determining the number of the classes of piezoelectric symmetry, Hermann's theorem must certainly be taken into account since according to it, the symmetry of piezoelectric properties of the crystals of classes, say, 4 *mm* and 6 *mm* and of the textures of class ∞m is the same. Moreover, it can be shown that crystals of $\bar{6}$ and $\bar{6}m2$ classes constitute one class of piezoelectric symmetry, although the forms of tensor **d** for these classes are different.

A similar situation was met in discussing elastic symmetry classes (Sec. 52), so that no detailed explanations are needed here. The form of tensor **d** for crystals of class $\bar{6}$ cannot "deteriorate" at any rotation whatever of the coordinate system about axis X_3, since the direction of axes X_1 and X_2 is not defined in the $\bar{6}$ class by the symmetry elements of a crystal. However, by rotating the coordinate system about axis X_3 through a certain angle we can turn to zero one of the two independent components of tensor **d** and thus bring the tensor to the same form that it has for the crystals of class $\bar{6}m2$. This proves that the true symmetry of this tensor is $\bar{6}m2$.

It must be borne in mind that belonging of a given particular crystal to one of the piezoelectric classes does not mean that this crystal actually displays piezoelectric properties. Some dielectric crystals belonging to the piezoelectric classes do not reveal, up to the attained accuracy of experiments, any piezoelectric properties. This is the difference between piezoelectricity and elasticity or thermal expansion which are characteristic of all solids. On the contrary the belonging of a crystal to one of the non-piezoelectric classes, is a reliable guarantee of the absence of any piezoelectric properties in this crystal.

Individual varieties of the piezoelectric effect are permissible for some piezoelectric classes and forbidden for others. Such is, for instance, the piezoelectric effect developing in case of uniform hydrostatic pressure. From equation (58.4) with $\sigma_{kl} = -p\delta_{kl}$, we have

$$D_i = -4\pi d_{ikk}p. \tag{58.5}$$

Thus, piezoelectric polarization appears in this case only when components $d_i = d_{ikk}$ of vector $\boldsymbol{d} = \mathbf{d} : \mathbf{I}$ differ from zero. Apparently $\boldsymbol{d}$ is a matter vector, and matter vectors differ from zero only when they specify the properties of crystals of pyroelectric classes. Therefore the piezoelectric effect appearing under uniform hydrostatic pressure is possible only in 10 crystallographic and 2 limit classes out of 20 crystallographic and 3 limit classes that permit the piezoelectric effect at all (Table 58.1).

Another instance relates to the experiments of the Curie brothers in which the piezoelectric effect was revealed: a load was placed on a crystal face, and the density of charge ρ_{surf} on this face was measured. Since the stress was just a uniaxial compression $\sigma_{kl} =$

Table 58.1

Vector of the Piezoelectric Effect Under Hydrostatic Pressure $d = \mathbf{d} : \mathbf{I}$ ($d_i = d_{ikk}$)

Classes	Vector d
1	$(d_{11}+d_{12}+d_{13})\,\boldsymbol{e}_1+(d_{21}+d_{22}+d_{23})\,\boldsymbol{e}_2+(d_{31}+d_{32}+d_{33})\,\boldsymbol{e}_3$
m ($m \perp \boldsymbol{e}_2$)	$(d_{11}+d_{12}+d_{13})\,\boldsymbol{e}_1+(d_{31}+d_{32}+d_{33})\,\boldsymbol{e}_3$
m ($m \perp \boldsymbol{e}_3$)	$(d_{11}+d_{12}+d_{13})\,\boldsymbol{e}_1+(d_{21}+d_{22}+d_{23})\,\boldsymbol{e}_2$
2 ($2 \parallel \boldsymbol{e}_2$)	$(d_{21}+d_{22}+d_{23})\,\boldsymbol{e}_2$
2 ($2 \parallel \boldsymbol{e}_3$), $mm2$	$(d_{31}+d_{32}+d_{33})\,\boldsymbol{e}_3$
3, 4, 6, ∞, $3m$, $4mm$, $6mm$, ∞m	$(2d_{31}+d_{33})\,\boldsymbol{e}_3$

$= -pn_kn_l$ ($\boldsymbol{n}$ is the unit vector of the perpendicular to the face), then

$$\rho_{\text{surf}} = -\frac{1}{4\pi}\,\boldsymbol{n}\cdot\boldsymbol{D} = pd_{ikl}n_in_kn_l. \tag{58.6}$$

It is evident that with such measurements only the symmetric part of tensor d_{ikl}—the tensor of the longitudinal piezoelectric effect is revealed

$$f_{ikl} = d_{(ikl)} = \frac{1}{3}\,(d_{ikl}+d_{kli}+d_{lik}). \tag{58.7}$$

In fact, $\boldsymbol{n}\cdot\mathbf{d} : \boldsymbol{nn} = \boldsymbol{n}\cdot\mathbf{f} : \boldsymbol{nn}$. The internal symmetry of tensor $\mathbf{f}$ is $[V^3]$. In distinction from tensor $\mathbf{d}$ it has in a general case not 18, but only 10 independent components. Its relation to tensor $\mathbf{d}$ is shown in Table 58.2. The coincidence of tensors $\mathbf{f}$ and $\mathbf{d}$ in some classes shows that in crystals of these classes all the components of tensor $\mathbf{d}$ can be obtained from the measurements of the longitudinal piezoelectric effect. In those cases when tensors $\mathbf{f}$ and $\mathbf{d}$ in crystals of a given class are different, it is quite impossible to obtain all the components of tensor $\mathbf{d}$ by means of such measurements alone. In the piezoelectric classes 422,622, $\infty 2$ the longitudinal piezoelectric effect is forbidden. The classes of the longitudinal piezoelectric symmetry are listed in Table 58.3. It can be seen that some crystallographic classes relating to different classes of piezoelectric symmetry are included in one and the same class of the longitudinal piezoelectric symmetry. Most interesting among them is class $\bar{4}3\,m$ of the longitudinal piezoelectric symmetry: it includes crystals of classes $\bar{4}3\,m$, 23, $\bar{4}2\,m$, $\bar{4}$ and 222 belonging in three different systems. Many piezoelectric crystals important for technology belong to the above

Table 58.2

The Connection of Tensor f of the Longitudinal Piezoelectric Effect with the Tensor of the Piezoelectric Coefficients for All Classes of Crystal Symmetry and of Textures Permitting the Piezoelectric Effect (the Location of Components f_{ikl} is the Same as in Table E.10)

Classes	f_{ikl}			
1	d_{11} $1/3\,(d_{21}+d_{16})$ $1/3\,(d_{31}+d_{15})$	$1/3\,(d_{12}+d_{26})$ d_{22} $1/3\,d_{32}+d_{24})$	$1/3\,(d_{13}+d_{35})$ $1/3\,(d_{23}+d_{34})$ d_{33}	$1/6\,(d_{14}+d_{25}+d_{36})$
2 $(2 \parallel X_2)$	0 $1/3\,(d_{21}+d_{16})$ 0	0 d_{22} 0	0 $1/3\,(d_{23}+d_{34})$ 0	$1/6\,(d_{14}+d_{25}+d_{36})$
2 $(2 \parallel X_3)$	0 0 $1/3\,(d_{31}+d_{15})$	0 0 $1/3\,(d_{32}+d_{24})$	0 0 d_{33}	$1/6\,(d_{14}+d_{25}+d_{36})$
m $(m \perp X_2)$	d_{11} 0 $1/3\,(d_{31}+d_{15})$	$1/3\,(d_{12}+d_{26})$ 0 $1/3\,(d_{32}+d_{24})$	$1/3\,(d_{13}+d_{35})$ 0 d_{33}	0
m $(m \perp X_3)$	d_{11} $1/3\,(d_{21}+d_{16})$ 0	$1/3\,(d_{12}+d_{26})$ d_{22} 0	$1/3\,(d_{13}+d_{35})$ $1/3\,(d_{23}+d_{34})$ 0	0
222	0 0 0	0 0 0	0 0 0	$1/6\,(d_{14}+d_{25}+d_{36})$
$mm2$	0 0 $1/3\,(d_{31}+d_{15})$	0 0 $1/3\,(d_{32}+d_{24})$	0 0 d_{33}	0
3	d_{11} $-d_{22}$ $1/3\,(d_{31}+d_{15})$	$-d_{11}$ d_{22} $1/3\,(d_{31}+d_{15})$	0 0 d_{33}	0
32, $\bar{6}2m$ $(2 \parallel X_1)$	d_{11} 0 0	$-d_{11}$ 0 0	0 0 0	0
32, $\bar{6}m2$ $(2 \parallel X_2,$ $m \perp X_1)$	0 $-d_{22}$ 0	0 d_{22} 0	0 0 0	0

Table 58.2 (cont'd)

Classes	f_{ikl}			
$3m$ ($m \perp X_1$)	0 $-d_{22}$ $^1/_3(d_{31}+d_{15})$	0 d_{22} $^1/_3(d_{31}+d_{15})$	0 0 d_{33}	0
$\bar{6}$	d_{11} $-d_{22}$ 0	$-d_{11}$ d_{22} 0	0 0 0	0
$\bar{4}$	0 0 $^1/_3(d_{31}+d_{15})$	0 0 $-^1/_3(d_{31}+d_{15})$	0 0 0	$^1/_6(2d_{14}+d_{36})$
$\bar{4}2m$	0 0 0	0 0 0	0 0 0	$^1/_6(2d_{14}+d_{36})$
4, 6, ∞ $4mm$, $6mm$, ∞m	0 0 $^1/_3(d_{31}+d_{15})$	0 0 $^1/_3(d_{31}+d_{15})$	0 0 d_{33}	0
23, $\bar{4}3m$	0 0 0	0 0 0	0 0 0	$^1/_2 d_{14}$

Note. **In all** centrosymmetric classes as well as **in classes** $\infty\infty$, **432, 622, 422,** $\infty 2$ **tensor f = 0.**

The Table gives coefficients $f_{i\lambda}$ connected **with coefficients** f_{ikl} **of the longi**tudinal **piezoelectric** effect tensor by the **recalculation rule**

$$f_{i\lambda} = \begin{cases} f_{ikl} & (kl \leftrightarrow \lambda = 1, 2, 3), \\ 2f_{ikl} & (kl \leftrightarrow \lambda = 4, 5, 6). \end{cases}$$

classes. A highly important ferroelectric-piezoelectric, Rochelle salt, is crystallized in class 222, the widely used crystals of potassium dihydrophosphate (KDP), ammonium dihydrophosphate (ADP) and all the family isomorphous to them are crystallized in class $\bar{4}2m$. Class $\bar{4}3m$ is especially interesting by piezoelectric semiconductors belonging to it, such as sphalerite, gallium arsenide, indium antimonide and others. Bismuth germanate much widely used in technology, is crystallized in class 23.

The tensor of the longitudinal piezoelectric effect for the crystals of these classes has only one independent component and is a mul-

Table 58.3

Symmetry of the Longitudinal Piezoelectric Effect

Crystals with longitudinal piezoelectric symmetry	Crystals in which the longitudinal piezoelectric effect has this symmetry
1	1
m	m
$mm2$	2, $mm2$
$3m$	3, $3m$
$\bar{6}m2$	32, $\bar{6}$, $\bar{6}m2$
∞m	4, 6, ∞, $4mm$, $6mm$, ∞m
$\bar{4}3m$	222, $\bar{4}$, $\bar{4}2m$, 23, $\bar{4}3m$

tiple of a unit septor S^0 $[\bar{4}3m]$ (see Table 47.4); its representation surface shown in Fig. 47.3 thus serves as a universal representation surface of the longitudinal piezoelectric effect for all such crystals. The longitudinal piezoelectric effect in direction $\boldsymbol{n}$ is determined with the aid of stereographic projection (Fig. 47.3) by the formula

$$f(\boldsymbol{n}) = f_{ijk} n_i n_j n_k = 2 f_{123} S^0(\boldsymbol{n}) / \sqrt{3} \tag{58.8}$$

Tensor **f** also has one independent component for the class of longitudinal piezoelectric symmetry $\bar{6}m2$ which includes crystals of classes $\bar{6}m2$ and 32; it is a multiple of a unit septor $S^0[\bar{6}m2]$ (see Table 47.3) whose representation surface (see Fig. 47.4) is also a universal representation surface of the longitudinal piezoelectric effect for the crystals of corresponding classes. The longitudinal piezoelectric effect is determined in this case with the aid of a stereographic projection (Fig. 47.4) and formula

$$f(\boldsymbol{n}) = -f_{222} S^0(\boldsymbol{n}). \tag{58.9}$$

For class ∞m of the longitudinal piezoelectric symmetry

$$f_{ijl} = F_V V^0{}_{(i}\delta_{jl)} + F_S S^0_{ijl}, \tag{58.10}$$

where the irreducible unit tensors of the ∞m symmetry are the vector $\boldsymbol{V}$ and septor **S** defined by equalities*

$$V^0_i = k_i, \tag{58.11}$$

$$S^0_{ijl} = \frac{1}{2}(5k_i k_j k_l - 3k_{(i}\delta_{jl)}) \tag{58.12}$$

* Cf. Table 47.4 and formulas (52.10) and (52.11).

(**k** is the unit vector of axis X_3), and the coefficients of the unit tensors are

$$F_V = \frac{3}{5}(f_{333} + 2f_{113}), \quad F_S = \frac{2}{5}(f_{333} - 3f_{113}). \tag{58.13}$$

The representation surfaces of the longitudinal piezoelectric effect for crystals of this class of the longitudinal piezoelectric symmetry are the surfaces of revolution

$$f(\boldsymbol{n}) = F_V V^0(\boldsymbol{n}) + F_S S^0(\boldsymbol{n}), \tag{58.14}$$

where $V^0(\boldsymbol{n})$ and $S^0(\boldsymbol{n})$ are the representation surfaces of the unit vector and unit septor whose sections are shown in Fig. 47.1. Depending on the ratio of coefficients F_V and F_S, the surfaces can have

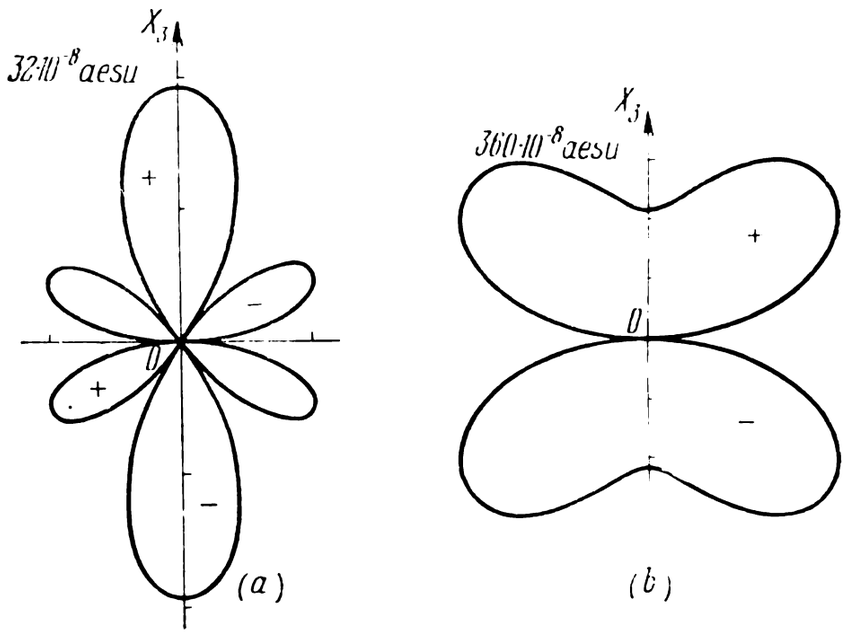


Fig. 58.1. Sections of the representation surfaces of the longitudinal piezoelectric effect being the surfaces of revolution: (a) for a cadmium sulphide crystal, CdS, class $6mm$; (b) for a barium titanate crystal, $BaTiO_3$, class $4mm$. Symmetry of the surfaces is ∞m, antisymmetry is $\infty/m'm$ (see Sec. 68). (Butabayev and Sirotin, 1972)

a septor or a vector character; to the first type belongs, for example, the representation surface of the longitudinal piezoelectric effect in cadmium sulphide, CdS (class $6mm$); to the second type that in barium titanate, $BaTiO_3$ (class $4mm$), Fig. 58.1. Both these crystals are widely used in technology.

If the representation surface of the longitudinal piezoelectric effect is not a surface of revolution it is more convenient to represent it by means of stereographic projections (see Sec. 24). Thus two stereographic projections and the section of the representation surface of the longitudinal piezoelectric effect in a tourmaline crystal (class $3m$) are shown in Fig. 44.2. Stereographic projections of the

representation surfaces of the longitudinal piezoelectric effect in two crystals of the monoclinic system are given in Figs. 58.2 and 58.3.

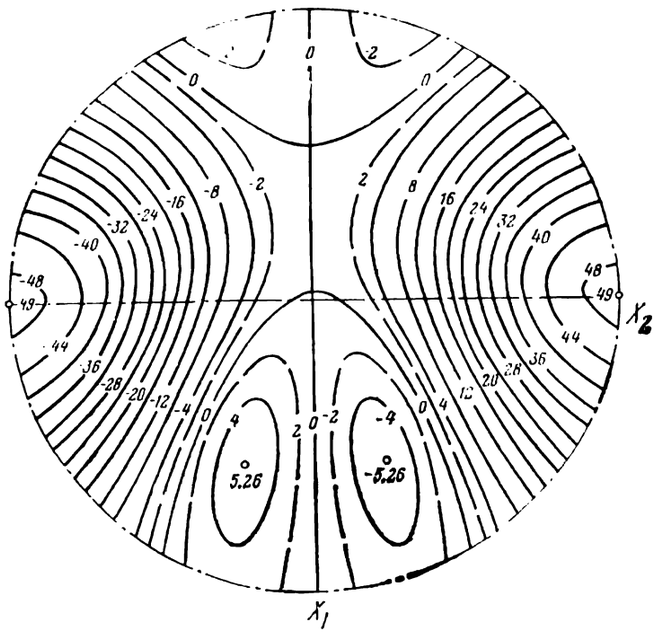


Fig. 58.2. Stereographic projection of the representation surface of the longitudinal piezoelectric effect in a lithium sulphate crystal, $Li_2SO_4 \cdot H_2O$, class 2. Symmetry of the surface is $mm2$, antisymmetry is mmm', in 10^{-8} aesu

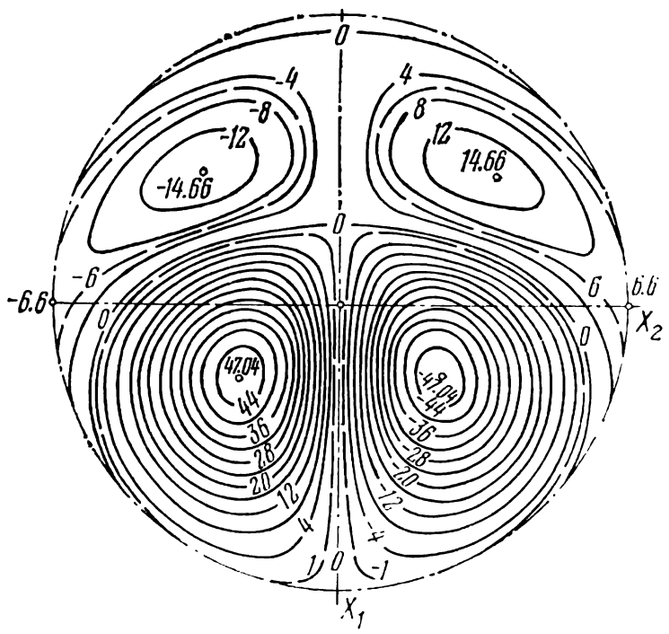


Fig. 58.3. Stereographic projection of the representation surface of the longitudinal piezoelectric effect in a crystal of ethylene diamine tartrate, class 2. Symmetry of the surface is $mm2$, antisymmetry is mmm'; in 10^{-8} aesu

The entirely different nature of the anisotropy of these crystals, belonging to the same class 2, is remarkable. The symmetry of the longitudinal piezoelectric effect in these crystals is $mm2$; the sym-

metry planes passing through the two-fold axis can be seen in Figs. 58.2 and 58.3, but they could have been seen much better, if the two-fold axis were brought into the centre of projection.

When examining the influence of crystal symmetry on their piezoelectric properties, we used the general forms of the piezoelectric coefficients tensor **d** computed for different crystallographic classes. Some results of this examination, however, can be obtained without any computations on the basis of only the Curie principle and Hermann's theorem. This is just what we shall do.

For the electric polarization to develop in a crystal (or generally in any homogeneous medium) under the influence of some external forces, it is necessary for a crystal, subjected to such influence, to have at least one singular polar direction, and for this it is necessary, in its turn (see Secs. 3, 25 and Appendix C), that the symmetry group of the medium under external influence should be $\infty\, m$ or any of its subgroups

$$\infty\, m \supseteq G_{\text{med. infl}}. \tag{58.15}$$

But the symmetry group of the medium under the influence should be according to the Gurie principle, not lower than the intersection (common part) of two groups: i.e. of the symmetry group of the free medium G_{med} and the symmetry group of influence G_{infl}:

$$G_{\text{med.infl}} \supseteq G_{\text{med}} \cap G_{\text{infl}}. \tag{58.16}$$

Comparing relations (58.15) and (58.16), we finally have

$$\infty\, m \supseteq G_{\text{med}} \cap G_{\text{infl}} \tag{58.17}$$

i.e. for the electric polarization to develop in a homogeneous medium under some external influence it is necessary that the intersection of the symmetry group of the medium and the symmetry group of the influence be group $\infty\, m$ or one of its subgroups.

This general rule is valid for all kinds of electric polarization. In piezoelectric polarization, the symmetry of the influence in expression (58.17) is described by one of the three groups: $\infty\, \infty\, m$ at uniform compression, ∞/mm at uniaxial extension, mmm in all other cases.

In a general case, when $G_{\text{infl}} = mmm$, the necessary condition for the development of piezoelectric polarization is as follows:

$$\infty\, m \supseteq G_{\text{med}} \cap mmm. \tag{58.18}$$

Since group mmm is centrosymmetric and group $\infty\, m$ is non-centrosymmetric, condition (58.18) is satisfied only by non-centrosymmetric group G_{med}: the piezoelectric homogeneous media are non-centrosymmetric.

But do all the non-centrosymmetric groups G_{med} satisfy condition (58.18)? At least one of them, namely $\infty\, \infty$, does not satisfy it. In fact, $\infty\, \infty \cap mmm = 222$, but this group is not a subgroup of group $\infty\, m$ at all. Thus piezoelectric polarization is not possible in media with symmetry $\infty\, \infty$.

The problem of the possibility of piezoelectric polarization and piezoelectric effect in crystals of class 432 is solved quite differently. The stress is easily found at which $432 \cap mmm = 1$; it will suffice to apply it so that none of the symmetry axes of the stress tensor would coincide with any of the symmetry axes of the crystal. In spite of the fact that condition (58.18) is satisfied here, a *linear* piezoelectric effect in crystals of the class 432 is impossible. Indeed, this effect is specified by a third-rank tensor. According to Hermann's theorem, the four-fold symmetry axes serve at the axes of the infinite order for this tensor. Hence it is evident that crystals of class 432 do not differ from media of class $\infty\, \infty$ by the symmetry of the linear piezoelectric effect, and we have just seen that in the

latter piezoelectric polarization is forbidden. However, along with the linear piezoelectric effect a considerably weaker quadratic piezoelectric effect is possible at which the polarization depends quadratically on the stress tensor components (see Sec. 74):

$$D_i = 4\pi Q_{ijklm}\sigma_{jk}\sigma_{lm}. \tag{58.19}$$

Since the quadratic effect is defined by a fifth-rank tensor, while the 432 class crystals have no higher order of symmetry axes than the four-fold ones, Hermann's

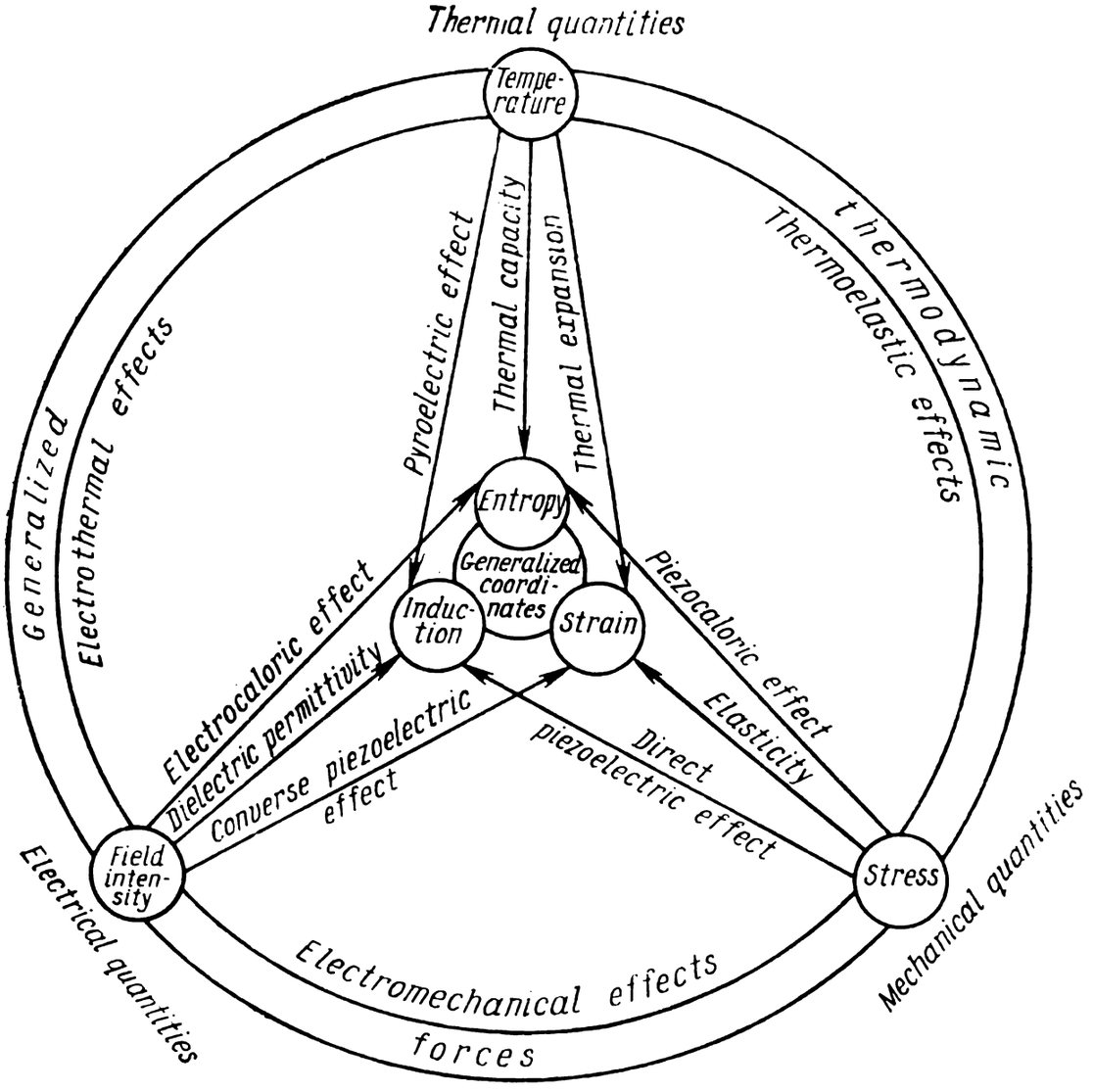


Fig. 58.4. Schematic diagram of interaction of thermal, electrical and mechanical phenomena in crystals

theorem is not applicable to this effect; consequently, the piezoelectric polarization of such a type is not forbidden by the principles of symmetry. Calculations show that a fifth-rank matter tensor Q of internal symmetry $V\,[[V^2]]^2$ for crystals of the class 432 can actually have non-zero components *.

It can be similarly shown that the longitudinal piezoelectric polarization in media with the symmetry $\infty\,2$ is forbidden by the Curie principle. The use of

* See Table E.23. The form of such tensors for the crystals of all classes was derived by Koptsik (1966).

Hermann's theorem will furnish a convincing proof of the linear longitudinal piezoelectric effect being forbidden also in crystals of classes 422 and 622.

Thus the bans imposed by the Curie principle and by vanishing of the components of a matter tensor do not coincide in essence. Forbidding the piezoelectric polarization in media with symmetry $\infty\ \infty$, the Curie principle completely eliminates the development in them of electric polarization as a result of mechanical stresses, irrespective of the character of functional dependence of polarization on stresses—whether it is linear, quadratic or still more complicated. On the contrary, the piezoelectric coefficients tensor being zero for a medium of definite symmetry only means that in this medium piezoelectric polarization linearly dependent on stresses is impossible, but the appearance of piezoelectric polarization related to stresses by more complicated functional dependence (e.g. quadratic dependence) is not excluded. This is convincingly illustrated by the quadratic piezoelectric effect in crystals of the class 432.

Taking into consideration the piezoelectric, the converse piezoelectric, the electrocaloric and the piezocaloric effects, we obtain an orderly diagram of the interaction between thermal, electrical and mechanical phenomena occurring in crystals: any generalized thermodynamic force applied to a crystal leads, generally speaking, to the alteration of all its generalized thermodynamic coordinates. The diagram, shown in Fig. 58.4 is borrowed, with some changes, from J. Nye's textbook (1957).

So the vanishing of a matter tensor leads to more concrete but less general bans, while the Curie principle leads to more general but less concrete ones. More concrete bans can be obtained, however, from the Curie principle (e.g. the ban of linear piezoelectric effect in crystals of class 432) if Hermann's theorem is used along with it. But in all cases it must be well remembered that the Curie principle, in combination with Hermann's theorem or without it, only forbids some effects but by no means states that the effects not opposing it actually exist.

The diagrammatic interactions of the thermal, electrical and mechanical properties of crystals are fully realized only in the absence of point symmetry, i.e. in crystals of class 1. Unfortunately there is not a single crystal yet of class 1 for which all the coefficients could be measured. Crystal symmetry results in the vanishing of some interactions or others. This is lucidly illustrated by the matrices in Table 58.4 (Nye, 1957).

Sec. 59. Simultaneous Solution of the Equations of Electro- and Elastostatics of Crystals

The theory of elasticity and the electrostatics are, strictly speaking, inapplicable to piezoelectric crystals as separate theories. Any change of the electrical state in a piezoelectric crystal changes its mechanical state and vice versa, and these changes must obey the equations of electrostatics and the theory of elasticity respectively. Therefore to determine the strength and induction of electric field, as well as stresses and strains in a crystal it is necessary to solve a system of equations

$$\operatorname{div} \boldsymbol{D} = 0, \qquad \operatorname{curl} \boldsymbol{E} = 0 \tag{59.1}$$

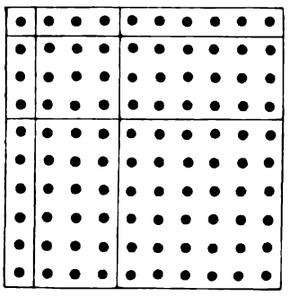
$$\operatorname{Div} \sigma = 0, \qquad \operatorname{Inc} \varepsilon = 0 \tag{59.2}$$

Table 58.4

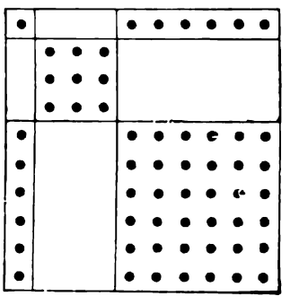
Thermodynamic Matrices *M* for All Crystallographic and Limit Classes

Triclinic system

class 1

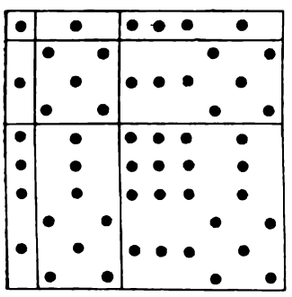


class $\bar{1}$

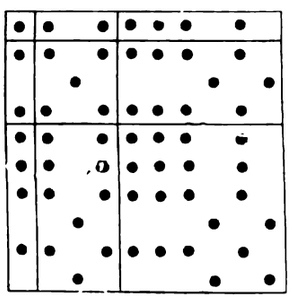


Monoclinic system

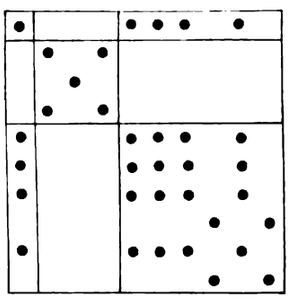
class 2



class *m*

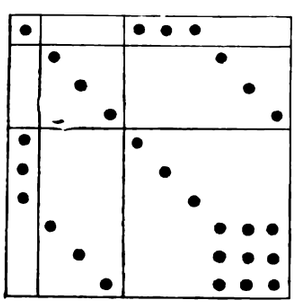


class 2/*m*

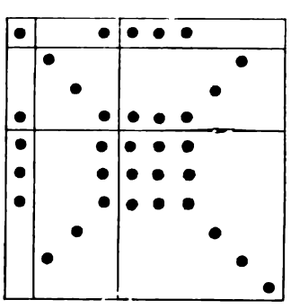


Rhombic system

class 222



class *mm*2



class *mmm*

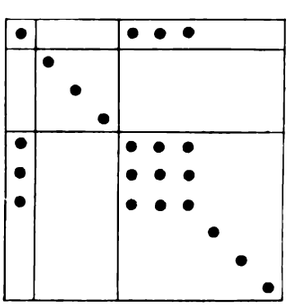
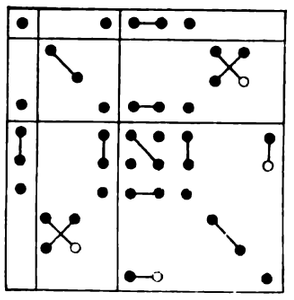


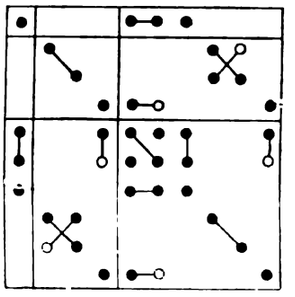
Table 58.4 (cont'd)

Tetragonal system

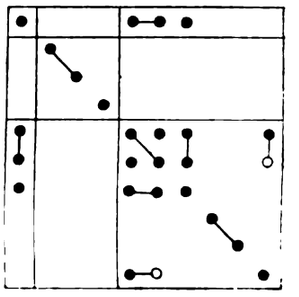
class 4



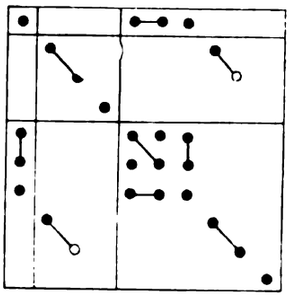
class $\bar{4}$



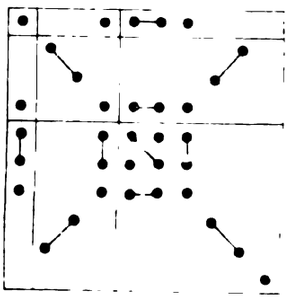
class $4/m$



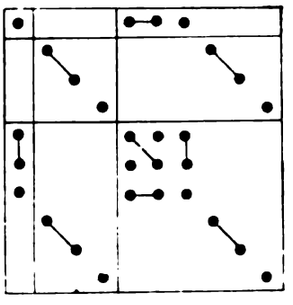
class 422



class $4mm$



class $42\ m$



class $4/mmm$

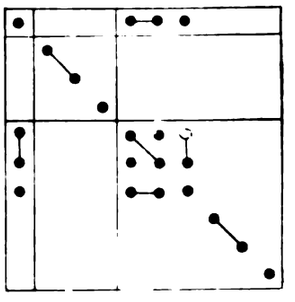
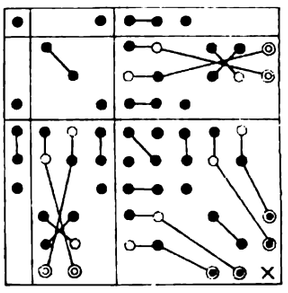


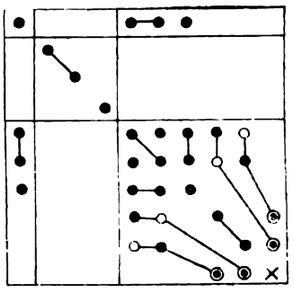
Table 58.4 (cont'd)

Trigonal system

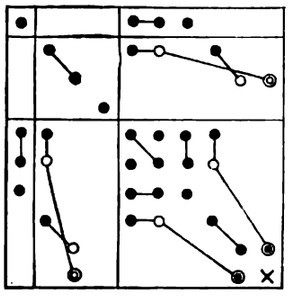
class 3



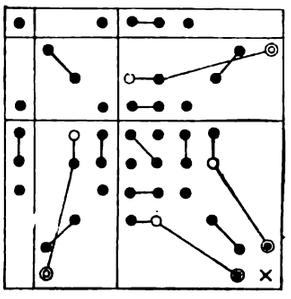
class $\bar{3}$



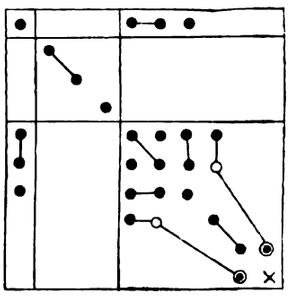
class 32



class $3m$

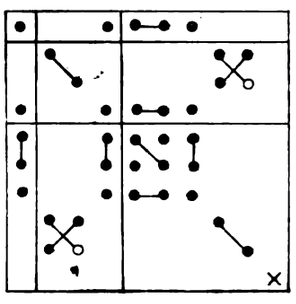


class $\bar{3}m$

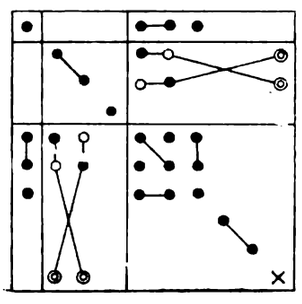


Hexagonal system and textures

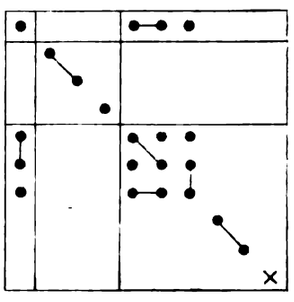
classes 6 and ∞



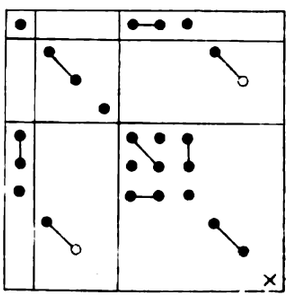
class $\bar{6}$



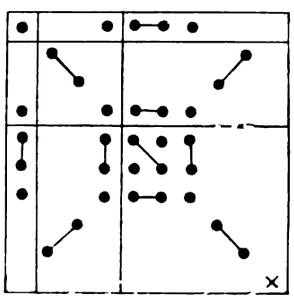
classes $6/m$, $6/mmm$ ∞/m and ∞/mm



classes 622 and ∞ 2



classes $6mm$ and m ∞



classes $\bar{6}m$ 2

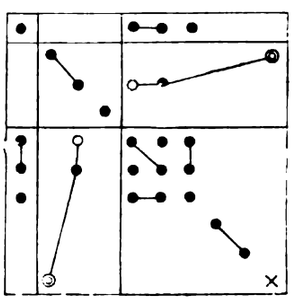
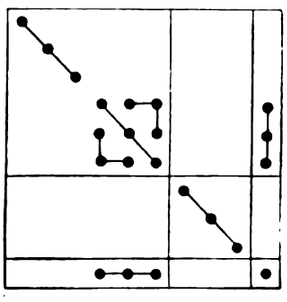


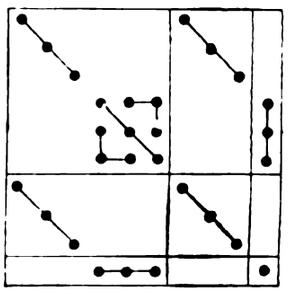
Table 58.4 (cont'd)

Cubic system

classes 23 and $\bar{4}3m$

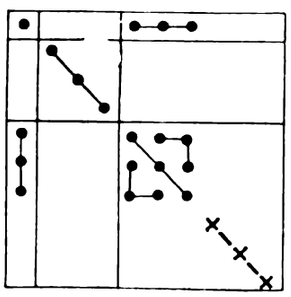


classes $m3$, 432 and $m3m$



Isotropic and gyrotropic bodies

classes $\infty\infty m$ and $\infty\infty$



Notation:

● non-zero component.

●—● equal components (different from zero).

●—○ components numerically equal, but opposite in sign.

◉ a component equal to twice the heavy dot component to which it is joined.

◎ a component equal to minus 2 times the heavy dot component to which it is joined.

× $2(s_{11}-s_{12}) = 2(M_{44}-M_{45})$.

All matrices are symmetric with respect to their principal diagonal.

with the corresponding electrical and mechanical boundary conditions, taking account of the connections between field tensors

$$\begin{aligned} \boldsymbol{D} &= \boldsymbol{\varkappa}\cdot\boldsymbol{E} + 4\pi\mathbf{d}:\sigma, \\ \varepsilon &= \boldsymbol{E}\cdot\mathbf{d} + \mathbf{s}:\sigma. \end{aligned} \tag{59.3}$$

It is just this connection that does not allow solving one of the systems (59.1) and (59.2) independently of the other.

The solution of a full system of equations of the electric and elastic equilibrium in elementary functions is possible only in some especially simple cases. Some of these cases that have practical importance and allow becoming acquainted with the peculiarities of the problem will be discussed here.

Piezoelectric Slab Under Homogeneous Mechanical Stresses. Let us consider a crystal slab whose thickness a is much less than its length and width: $a^2 \ll S$; this permits neglecting the effects at the edges. The orientation of the slab is specified by the unit vector of perpendicular $\boldsymbol{n}$; let us agree that the vector is directed from the lower to the upper side of the slab. The surfaces of the slab perpendicular to $\boldsymbol{n}$ are metal-coated. Uniform stress $\boldsymbol{\sigma}$ is applied to the slab. Let us find the strain and charge density on the plates.

Since the surfaces are metal-coated, they are equipotential. Having chosen the origin somewhere on the lower plate, we introduce coordinate $z = \boldsymbol{n}\cdot\boldsymbol{r}$. Apparently, all the planes parallel to the plates will be also equipotential surfaces, the potential φ depending only on z, i.e. $\varphi = \varphi(z)$. Then the electric field strength $\boldsymbol{E} = -\varphi'\boldsymbol{n}$, where $\varphi' = d\varphi/dz$.

To the plates of the slab forces $\boldsymbol{\sigma}\cdot\boldsymbol{n}$ and $-\boldsymbol{\sigma}\cdot\boldsymbol{n}$ are applied per unit area, and on the lateral surfaces force $\boldsymbol{\sigma}\cdot\boldsymbol{q}$, where $\boldsymbol{q}$ is a normal to the given piece of the lateral surface. The equations of elastic equilibrium and the boundary conditions for stresses are satisfied. Equations (59.3) can now have the form

$$\boldsymbol{D} = -\boldsymbol{\varkappa}\cdot\boldsymbol{n}\varphi' + 4\pi\mathbf{d}:\sigma, \tag{59.4}$$

$$\varepsilon = -\boldsymbol{n}\cdot\mathbf{d}\varphi' + \mathbf{s}:\sigma, \tag{59.5}$$

where φ' depends only on z, while $\boldsymbol{\sigma}$ does not depend on the coordinates at all. Therefore the equation $\operatorname{div}\boldsymbol{D} = 0$ leads to $\varphi'' = 0$. Hence it is clear that φ is a linear function of z, this meaning that the strains are homogeneous and, consequently, the equations of the compatibility of strains $\operatorname{Inc}\varepsilon = 0$ are identically satisfied.

When the plates are short-circuited, $\varphi(0) = \varphi(a)$. Hence $\varphi = \text{const}$, i.e. the field strength in the slab is zero. The density of the surface charges on the lower plate is

$$\rho_{\text{surf}} = \frac{1}{4\pi}\boldsymbol{n}\cdot\boldsymbol{D} = \boldsymbol{n}\cdot\mathbf{d}:\sigma. \tag{59.6}$$

On the upper plate it is the same in magnitude but opposite in sign (this is due to the opposite direction of the external normal to the surface). The strains in the slab in this case, according to (59.5), are equal to $\boldsymbol{\varepsilon} = \mathbf{s} : \boldsymbol{\sigma}$, i.e. they are the same as in the absence of the piezoelectric effect.

With the plates open the potential difference $U = \varphi(0) - \varphi(a) = -a\varphi'$ does not equal zero, and therefore the field in the slab is also non-zero. On the other hand with the plates open $\boldsymbol{n}\cdot\boldsymbol{D} = 0$. Taking this into account, we obtain from (59.4)

$$\varphi' = \frac{4\pi \boldsymbol{n}\cdot\mathbf{d} : \boldsymbol{\sigma}}{\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n}}, \tag{59.7}$$

from which we find the field strength $\boldsymbol{E} = -\varphi'\boldsymbol{n}$ and the potential difference at the plates $U = -a\varphi'$. The strain now depends not only on the elastic, but also on the piezoelectric properties of the crystal: according to (59.5)

$$\boldsymbol{\varepsilon} = -\frac{4\pi(\boldsymbol{n}\cdot\mathbf{d} : \boldsymbol{\sigma})\,\boldsymbol{n}\cdot\mathbf{d}}{\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n}} + \mathbf{s} : \boldsymbol{\sigma}.$$

This can be written thus

$$\boldsymbol{\varepsilon} = \left[\mathbf{s} - \frac{4\pi(\boldsymbol{n}\cdot\mathbf{d})(\boldsymbol{n}\cdot\mathbf{d})}{\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n}}\right] : \boldsymbol{\sigma}. \tag{59.8}$$

The expression in brackets plays the role of a new elastic compliance tensor which depends on the piezoelectric coefficients. Apparently, the stiffness of the slab in this case is somewhat increased; nothing to wonder at: the work of the forces applied to the slab surface is now spent not only to produce the elastic strain energy

$$W_{\text{elast}} = \frac{1}{2} a\boldsymbol{\sigma} : \boldsymbol{\varepsilon} = \frac{1}{2} a\boldsymbol{\sigma} : \left[\mathbf{s} - \frac{4\pi(\boldsymbol{n}\cdot\mathbf{d})(\boldsymbol{n}\cdot\mathbf{d})}{\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n}}\right] : \boldsymbol{\sigma} =$$

$$= \frac{1}{2} a\boldsymbol{\sigma} : \mathbf{s} : \boldsymbol{\sigma} - \frac{1}{2} a \frac{4\pi(\boldsymbol{n}\cdot\mathbf{d}\cdot\boldsymbol{\sigma})^2}{\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n}}$$

per 1 cm² of the slab, but also to produce electric energy*

$$W_{\text{el}} = \frac{1}{2} CU^2 = \frac{1}{2}\frac{\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n}}{4\pi a}\left(\frac{4\pi a\boldsymbol{n}\cdot\mathbf{d} : \boldsymbol{\sigma}}{\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n}}\right)^2 = \frac{1}{2} a \frac{4\pi(\boldsymbol{n}\cdot\mathbf{d}\cdot\boldsymbol{\sigma})^2}{\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n}}$$

per 1 cm². Thus, the strain diminishes just enough for the associated decrease of elastic energy to compensate for the appearance of electric energy.

The ratio $W_{\text{el}}/(W_{\text{elast}} + W_{\text{el}})$ shows what part of the mechanical energy $R_{\text{mech}} = W_{\text{elast}} + W_{\text{el}}$ spent on straining the piezoelectric slab becomes converted into electrical energy; the square root of this ratio

$$k = \sqrt{W_{\text{el}}/R_{\text{mech}}} \tag{59.9}$$

* Here C is the capacity per 1 cm² of the slab (see Sec. 28).

is called the *coefficient of the electromechanical coupling.* It can be represented as

$$k^2 = \frac{4\pi\,(\boldsymbol{E}\cdot\mathbf{d}:\sigma)^2}{(\boldsymbol{E}\cdot\varkappa\cdot\boldsymbol{E})\,(\sigma:\mathbf{s}:\sigma)}. \tag{59.10}$$

Obviously this ratio does not depend on the magnitude of the electric field or mechanical stresses: if all the components of vector $\boldsymbol{E}$ or tensor σ are increased several times, the ratio will not change. However, due to the anisotropy of the crystal, it essentially depends on the direction of the electric field and the orientation of the stress tensor.

In actual practice a uniformly stressed state of a piezoelectric slab is usually realized in the form of uniaxial extension or compression, the direction of which is either perpendicular to the slab (*a longitudinal piezoelectric effect*) or lies in its plane (*a transversal effect*).

In case of the longitudinal effect the stress tensor $\sigma = \sigma\boldsymbol{nn}$. The charge surface density on short-circuited plates is

$$\rho_{\text{surf}} = \sigma\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{nn}, \tag{59.11}$$

the potential difference across the plates in the open circuit is

$$U = 4\pi a\sigma\,\frac{\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{nn}}{\boldsymbol{n}\cdot\varkappa\cdot\boldsymbol{n}}. \tag{59.12}$$

Comparing the stress σ with the relative change of the slab thickness $\boldsymbol{n}\cdot\varepsilon\cdot\boldsymbol{n}$, we obtain Young's modulus $E\,(\boldsymbol{n})$. In conducting plates its magnitude is the same as in the absence of the piezoelectric effect, while in non-conducting plates (cf. (59.8))

$$\frac{1}{E\,(\boldsymbol{n})} = \boldsymbol{nn}:\mathbf{s}:\boldsymbol{nn}\left[1 - \frac{4\pi\,(\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{nn})^2}{(\boldsymbol{n}\cdot\varkappa\cdot\boldsymbol{n})\,(\boldsymbol{nn}:\mathbf{s}:\boldsymbol{nn})}\right]. \tag{59.13}$$

The fraction in brackets apparently represents the square of the coefficient of electromechanical coupling for the case of the longitudinal piezoelectric effect (cf. (59.12)). Since in all formulas describing the longitudinal effect tensor $\mathbf{d}$ occurs only in combinations $\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{nn}$, it can be replaced by the tensor of the longitudinal piezoelectric effect $f_{ijk} = f_{(ijk)}$; indeed, at any $\boldsymbol{n}$ we have $\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{nn} = \boldsymbol{n}\cdot\mathbf{f}:\boldsymbol{nn}$. The symmetry of tensor $\mathbf{f}$ was discussed in detail in Sec. 58.

Under transversal effect the stress tensor $\sigma = \sigma\boldsymbol{qq}$, where $\boldsymbol{q}$ is the unit vector coplanar to the plane of the slab. In this case the surface density of the charge on the conducting plates is

$$\rho_{\text{surf}} = \sigma\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{qq} \tag{59.14}$$

and the potential difference across the non-conducting plates is

$$U = 4\pi a\sigma\,\frac{\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{qq}}{\boldsymbol{n}\cdot\varkappa\cdot\boldsymbol{n}}. \tag{59.15}$$

The coefficient of the electromechanical coupling under transversal effect

$$k^2 = \frac{4\pi\,(\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{qq})^2}{(\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n})\,(\boldsymbol{qq}:\mathbf{s}:\boldsymbol{qq})} \tag{59.16}$$

for each given section (i.e. at a certain fixed $\boldsymbol{n}$) depends on the direction of the extension $\boldsymbol{q}$.

Piezoelectric Slab at a Potential Difference. Let us apply a potential difference U to the plates of the same piezoelectric slab. Evidently, a field $\boldsymbol{E} = (U/a)\,\boldsymbol{n}$ will develop in the slab. If the slab is free, i.e. the forces on its plates and lateral surface are zero, the stresses throughout the slab will also be zero. Then

$$\boldsymbol{D} = (U/a)\,\boldsymbol{\varkappa}\cdot\boldsymbol{n}, \tag{59.17}$$

$$\boldsymbol{\varepsilon} = (U/a)\,\boldsymbol{n}\cdot\mathbf{d}, \tag{59.18}$$

whence we find the charge density on the lower plate

$$\rho_{\text{surf}} = \frac{1}{4\pi}\boldsymbol{n}\cdot\boldsymbol{D} = \frac{U}{4\pi a}\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n}. \tag{59.19}$$

The mechanical analogue of a slab with non-conducting plates is a slab to which uniaxial compression or tensile stress $\boldsymbol{\sigma} = \sigma\boldsymbol{nn}$ is applied that prevents any change in its thickness, so that $\boldsymbol{\varepsilon} : \boldsymbol{nn} = 0$ all the time. From equation

$$\boldsymbol{\varepsilon} : \boldsymbol{nn} = (U/a)\,\boldsymbol{n}\cdot\mathbf{d} : \boldsymbol{nn} + \sigma\boldsymbol{nn} : \mathbf{s} : \boldsymbol{nn} = 0$$

we find the stress magnitude

$$\sigma = -\frac{U}{a}\,\frac{\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{nn}}{\boldsymbol{nn}:\mathbf{s}:\boldsymbol{nn}}. \tag{59.20}$$

whence the expression for induction is

$$\boldsymbol{D} = \frac{U}{a}\left[\boldsymbol{\varkappa}\cdot\boldsymbol{n} - \frac{4\pi\,(\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{nn})\,\mathbf{d}:\boldsymbol{nn}}{\boldsymbol{nn}:\mathbf{s}:\boldsymbol{nn}}\right].$$

This can be represented in the form

$$\boldsymbol{D} = \left[\boldsymbol{\varkappa} - \frac{4\pi\,(\mathbf{d}:\boldsymbol{nn})\,(\mathbf{d}:\boldsymbol{nn})}{\boldsymbol{nn}:\mathbf{s}:\boldsymbol{nn}}\right]\cdot\boldsymbol{E}, \tag{59.21}$$

similar to (59.8): the expression in brackets playing the role of the changed dielectric permittivity tensor. The charge densities on the plates

$$\rho_{\text{surf}} = \frac{\boldsymbol{n}\cdot\boldsymbol{D}}{4\pi} = \frac{U\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n}}{4\pi a}\left[1 - \frac{4\pi\,(\boldsymbol{n}\cdot\mathbf{d}:\boldsymbol{nn})^2}{(\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n})\,(\boldsymbol{nn}:\mathbf{s}:\boldsymbol{nn})}\right] \tag{59.22}$$

are less than in the case of a free slab (59.19). The density decrease is determined by the square of the electromechanical coupling coefficient k^2, as in (59.13). The same coefficient k^2 shows what part

of the electric energy, spent to produce the potential difference

$$R_{\text{el}} = \frac{1}{2} CU^2 = \frac{U^2}{8\pi a} \boldsymbol{n} \cdot \boldsymbol{\varkappa} \cdot \boldsymbol{n}$$

is converted into the mechanical stress energy

$$W_{\text{mech}} = \frac{1}{2} a\boldsymbol{\sigma} : \mathbf{s} : \boldsymbol{\sigma}$$

(both these quantities relate to 1 cm^2 of the slab). In point of fact

$$k^2 = \frac{W_{\text{mech}}}{R_{\text{el}}} = \frac{4\pi (\boldsymbol{n} \cdot \mathbf{d} : \boldsymbol{nn})^2}{(\boldsymbol{n} \cdot \boldsymbol{\varkappa} \cdot \boldsymbol{n}) (\boldsymbol{nn} : \mathbf{s} : \boldsymbol{nn})}. \tag{59.23}$$

Piezoelectric Crystal at a Hydrostatic Pressure. An exact solution of this problem is only possible for crystals of a spherical form. Let a piezoelectric sphere of radius R, with tensors of dielectric permittivity $\boldsymbol{\varkappa}$, and piezoelectric coefficients $\mathbf{d}$ be submerged in a non-conducting liquid with dielectric permittivity $\varkappa_0$, the pressure in which equals p. The liquid fills all the space surrounding the crystal. The equations of elastic equilibrium div $\boldsymbol{\sigma} = 0$ and the boundary conditions for stresses ($\boldsymbol{\sigma} \cdot \boldsymbol{n} = \boldsymbol{\sigma}_0 \cdot \boldsymbol{n}$, where $\boldsymbol{\sigma}$ and $\boldsymbol{\sigma}_0$ are the stresses in the crystal and the liquid surrounding it, $\boldsymbol{n}$ is the unit vector of the normal to the crystal surface) are satisfied, if both in the liquid and in the crystal the stress tensor

$$\boldsymbol{\sigma} = -p\mathbf{I}. \tag{59.24}$$

The piezoelectric properties of the material are defined by vector $\boldsymbol{d} = \mathbf{d} : \mathbf{I}$ with components d_{ikk} (see Sec. 58). It is this very vector with which the vector of the piezoelectric dipole moment is collinear

$$\mathbf{M} = \mathbf{d} : \boldsymbol{\sigma} = -p\mathbf{d} : \mathbf{I} = -p\mathbf{d}. \tag{59.25}$$

The latter, as could be expected by the analogy with a pyroelectric sphere problem (see Sec. 31), defines the electric field potentials

$$\varphi^{(i)} = -\boldsymbol{r} \cdot \boldsymbol{\beta} \cdot \boldsymbol{M}, \quad \varphi^{(e)} = (R/r)^3 \boldsymbol{r} \cdot \boldsymbol{\gamma} \cdot \boldsymbol{M}$$

in the crystal and liquid respectively. The so-far-unknown constant tensors $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ are determined, as in Secs. 28 and 31, from the boundary conditions of the continuity of potential φ and the normal component of the vector $\boldsymbol{D}$ on the interface between the piezoelectric substance and the liquid. The tensors are found to be

$$\boldsymbol{\beta} = -\boldsymbol{\gamma} = -4\pi (\boldsymbol{\varkappa} + 2\varkappa_0 \mathbf{I})^{-1}.$$

whence the strength and induction* of the electric field in the crystal are

$$\boldsymbol{E}^{(i)} = -\operatorname{grad} \varphi^{(i)} = 4\pi p (\boldsymbol{\varkappa} + 2\varkappa_0 \mathbf{I})^{-1} \cdot \boldsymbol{d}, \tag{59.26}$$

$$\boldsymbol{D}^{(i)} = \boldsymbol{\varkappa} \cdot \boldsymbol{E}^{(i)} + 4\pi \boldsymbol{M} = -2\varkappa_0 \boldsymbol{E}^{(i)}. \tag{59.27}$$

* In calculating (59.27) for induction the same method as for the derivation of (28.27) is used.

When $\boldsymbol{E}$ and $\boldsymbol{\sigma}$ are known, the strains are easily calculated. Let us calculate, in particular, the relative change of the crystal volume

$$\frac{\Delta V}{V} = \boldsymbol{\varepsilon} : \mathbf{I} = -\frac{p}{K}\,[1 - 4\pi K \boldsymbol{d} \cdot (\boldsymbol{\varkappa} + 2\varkappa_0 \mathbf{I})^{-1} \cdot \boldsymbol{d}], \qquad (59.28)$$

where $K = (\mathbf{I} : \boldsymbol{s} : \mathbf{I})^{-1}$ is the modulus of uniform compression (see Sec. 53). In this case too, the stiffness of the crystal increases as a result of the piezoelectric effect. The role of the square of the electromechanical coupling coefficient, characterizing this increase, is played here by the second term in the square brackets of (59.28).

Sec. 60. Invariant and Non-Invariant Thermodynamic Potentials and Their Matrices

The internal energy of a crystal U and its thermodynamic potential Φ are the functions of three quantities: a scalar characterizing the thermal state of the crystal, a vector characterizing its electrical state, and a symmetric second-rank tensor characterizing its mechanical state. On the other hand, in thermodynamics there are two quantities of each of these types: scalars S and T, vectors $\widetilde{\boldsymbol{D}}$ and $\boldsymbol{E}$, tensors $\boldsymbol{\varepsilon}$ and $\boldsymbol{\sigma}$. The internal energy U serves as a thermodynamic

Table 60.1

Eight Invariant Thermodynamic Potentials

Notation and definition	Name	Total differential
U	internal energy	$dU = T\,dS + \boldsymbol{E} \cdot d\widetilde{\boldsymbol{D}} + \boldsymbol{\sigma} : d\boldsymbol{\varepsilon}$
$F = U - TS$	free energy	$dF = -S\,dT + \boldsymbol{E} \cdot d\widetilde{\boldsymbol{D}} + \boldsymbol{\sigma} : d\boldsymbol{\varepsilon}$
$H_{\text{el}} = U - \boldsymbol{E} \cdot \widetilde{\boldsymbol{D}}$	electric enthalpy	$dH_{\text{el}} = T\,dS - \widetilde{\boldsymbol{D}} \cdot d\boldsymbol{E} + \boldsymbol{\sigma} : d\boldsymbol{\varepsilon}$
$H_{\text{mech}} = U - \boldsymbol{\sigma} : \boldsymbol{\varepsilon}$	mechanical enthalpy	$dH_{\text{mech}} = T\,dS + \boldsymbol{E} \cdot d\widetilde{\boldsymbol{D}} - \boldsymbol{\varepsilon} : d\boldsymbol{\sigma}$
$H = U - \boldsymbol{E} \cdot \widetilde{\boldsymbol{D}} - \boldsymbol{\sigma} : \boldsymbol{\varepsilon}$	enthalpy	$dH = T\,dS - \widetilde{\boldsymbol{D}} \cdot d\boldsymbol{E} - \boldsymbol{\varepsilon} : d\boldsymbol{\sigma}$
$\Phi_{\text{mech}} = U - TS - \boldsymbol{\sigma} : \boldsymbol{\varepsilon}$	mechanical thermodynamic potential	$d\Phi_{\text{mech}} = -S\,dT + \boldsymbol{E} \cdot d\widetilde{\boldsymbol{D}} - \boldsymbol{\varepsilon} : d\boldsymbol{\sigma}$
$\Phi_{\text{el}} = U - TS - \boldsymbol{E} \cdot \widetilde{\boldsymbol{D}}$	electrical thermodynamic potential	$d\Phi_{\text{el}} = -S\,dT - \widetilde{\boldsymbol{D}} \cdot d\boldsymbol{E} + \boldsymbol{\sigma} : d\boldsymbol{\varepsilon}$
$\Phi = U - TS - \boldsymbol{E} \cdot \widetilde{\boldsymbol{D}} - \boldsymbol{\sigma} : \boldsymbol{\varepsilon}$	thermodynamic potential	$d\Phi = -S\,dT - \widetilde{\boldsymbol{D}} \cdot d\boldsymbol{E} - \boldsymbol{\varepsilon} : d\boldsymbol{\sigma}$

potential of the crystal with respect to the set S, $\tilde{D}$, ε, while the thermodynamic potential Φ plays the same role with respect to the set T, E, σ. There are $2^3 = 8$ such sets all in all, and correspondingly 8 invariant thermodynamic potentials. They are all derived from the internal energy by subtracting from it one, two or three of the following products:

$$TS, \quad E\cdot\tilde{D}, \quad \sigma : \varepsilon. \tag{60.1}$$

The invariance with respect to point group G of crystal symmetry follows from the fact that internal energy $U = U(S, \tilde{D}, \varepsilon)$ is invariant with respect to group G, while each of products (60.1) is invariant with respect to group $\infty\infty m \supset G$.

Let us consider, for instance, the potential $H_{el} = U - E\cdot D$ which is called the *electric enthalpy*. Its total differential is

$$dH_{el} = dU - E\cdot d\tilde{D} - \tilde{D}\cdot dE = TdS - \tilde{D}\cdot dE + \sigma : d\varepsilon, \tag{60.2}$$

whence it is clear that this is the thermodynamic potential with respect to the set S, E, ε. And indeed, it follows from (60.2) that

$$T = \frac{\partial H_{el}}{\partial S}, \quad \tilde{D} = -\frac{\partial H_{el}}{\partial E},$$

$$\sigma = \frac{\partial H_{el}}{\partial \varepsilon}. \tag{60.3}$$

The other potentials are obtained similarly. They are all given in Table 60.1. It should be borne in mind that neither the terms given in the Table, nor the notation is conventional*.

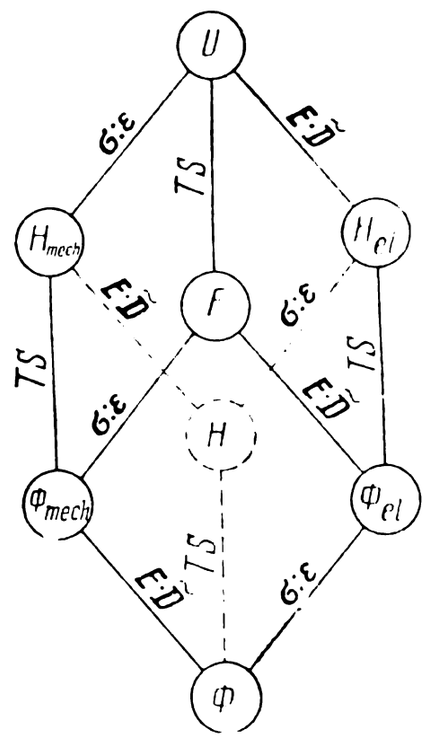


Fig. 60.1. Rhombohedron of thermodynamic potentials

The same eight potentials are shown in Fig. 60.1, which illustrates the way of obtaining these potentials and their interrelations. The potentials are located at the vertices of a rhombohedron. Its upper vertex is occupied by internal energy—the potential with respect to the generalized thermodynamic coordinates. Below are located three vertices occupied by potentials with respect to two coordinates and one force. Still lower are three vertices with potentials with respect to two forces and one coordinate. Finally, the lowest vertex is occupied by the thermodynamic potential Φ—a function of generalized thermodynamic forces. A definite physical meaning can also be ascribed to the edges: a forward descent along the edge means the subtraction of product TS, the descent to the right and backwards means subtraction of scalar product $E\cdot\tilde{D}$, the descent to the left and backwards means subtraction of biscalar product $\sigma\cdot\varepsilon$. Movement in the

* In particular, the thermodynamic potential Φ is sometimes called Gibbs free energy, while free energy F is called the Helmholtz free energy.

opposite directions would naturally mean addition of corresponding products. The opposite vertices of the rhombohedron are occupied by potentials related to the mutually supplementing sets of thermodynamic variables, for example U $(S, \tilde{D}, \varepsilon)$ and Φ (T, E, σ), or F $(T, \tilde{D}, \varepsilon)$ and H (S, E, σ).

There also exist non-invariant thermodynamic potentials. Such are, for instance, the function $U - E_1\tilde{D}_1$ which is the thermodynamic potential with respect to the set of variables S, E_1, $\tilde{D}_2$, $\tilde{D}_3$, ε_1, ε_2, ε_3, ε_4, ε_5, ε_6, and the function $U - TS - E_1\tilde{D}_1 - \sigma_2\varepsilon_2$ which is the thermodynamic potential with respect to the set T, E_1, $\tilde{D}_2$, $\tilde{D}_3$, ε_1, ε_2, ε_3, ε_4, ε_5, ε_6.

These potentials are more or less dependent on direction. For instance, the potential $U - E_1\tilde{D}_1$ depends on the choice of the unit vector $\boldsymbol{e}_1$: if it is chosen in a different way, the potential will change, generally speaking. However, the potential $U - E_1\tilde{D}_1$ does not depend on the choice of unit vectors $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$ in the plane perpendicular to the unit vector $\boldsymbol{e}_1$. The potential $U - TS - E_1\tilde{D}_1 - \sigma_2\varepsilon_2$ on the contrary, depends on the choice of two unit vectors: $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$, i.e. on the coordinate system on the whole.

The non-invariant potentials can be regarded as functions of not only the usual thermodynamic arguments, but also of one or several unit vectors $\boldsymbol{p}$, $\boldsymbol{q}$, ... Thus potential $U - E_1\tilde{D}_1$ represents particular value (when $\boldsymbol{p} = \boldsymbol{e}_1$) of the potential $U - (\boldsymbol{E}\cdot\boldsymbol{p})\ (\tilde{\boldsymbol{D}}\cdot\boldsymbol{p})$, and the potential $U - TS - E_1D_1 - \sigma_2\varepsilon_2$ is a particular value (when $\boldsymbol{p} = \boldsymbol{e}_1$, $\boldsymbol{q} = \boldsymbol{e}_2$) of $U - TS - (\boldsymbol{E}\cdot\boldsymbol{p})\ (\tilde{\boldsymbol{D}}\cdot\boldsymbol{p}) - (\boldsymbol{\sigma} : \boldsymbol{qq})\ (\boldsymbol{\varepsilon} : \boldsymbol{qq})$.

Let Ψ be any (not necessarily invariant) thermodynamic potential, and $\xi_1, \ldots, \xi_{10}$ its arguments (y_A or Y_A) reckoned from the initial state in which all the thermodynamic forces Y_A equal zero, and the crystal is neither strained nor polarized. Then the beginning of its expansion into a Taylor series appears as

$$\Psi = \Psi_0 + \frac{1}{2}\left(\frac{\partial^2\Psi}{\partial\xi_A\,\partial\xi_B}\right)_0 \xi_A\xi_B + \ldots \tag{60.4}$$

Depending on whether the argument ξ_A is thermodynamic coordinate or a force, one of the following equalities will hold

$$\xi_A = y_A, \quad Y_A = \left(\frac{\partial^2\Psi}{\partial\xi_A\,\partial\xi_B}\right)_0 \xi_B; \tag{60.5}$$

$$\xi_A = Y_A, \quad y_A = -\left(\frac{\partial^2\Psi}{\partial\xi_A\,\partial\xi_B}\right)_0 \xi_B. \tag{60.6}$$

Let matrix $\| (\partial^2\Psi/\partial\xi_A\partial\xi_B)_0 \|$ be the matrix of potential Ψ if Ψ is invariant and is located in the upper half of the rhombohedron of Fig. 60.1, or if Ψ is non-invariant and is obtained by subtracting not more than five products of the type $Y_A y_A$ from U. In all other

cases we shall consider the matrix of the potential Ψ to be $\| -(\partial^2\Psi/\partial\xi_A\partial\xi_B)_0 \|$.

Let us note some properties of such thermodynamic matrices. They are all symmetric. Any one of them can be used to approximately determine the corresponding potential by formula (60.4), thermodynamic force (60.5) or coordinate (60.6). Finally, the matrices of potentials Ψ and Ω with respect to the mutually supplementing sets of arguments $\xi_1, \ldots, \xi_{10}$ and $\zeta_1, \ldots, \zeta_{10}$ satisfy relations of the form

$$\left\| \left(\frac{\partial^2\Psi}{\partial\xi_A\,\partial\xi_D} \right)_0 \right\|^{-1} = \| E_{AB} \| \left\| -\left(\frac{\partial^2\Omega}{\partial\zeta_B\,\partial\zeta_C} \right)_0 \right\| \| E_{CD} \|, \qquad (60.7)$$

where $\| E_{AB} \|$ is a diagonal matrix, with plus and minus unities on its diagonal:

$$E_{AB} = \begin{cases} +\delta_{AB}, & \text{if} \quad \xi_A = y_A, \quad \zeta_A = Y_A, \\ -\delta_{AB}, & \text{if} \quad \xi_A = Y_A, \quad \zeta_A = y_A. \end{cases}$$

Thus, the matrix of a thermodynamic potential $\| M_{AB} \| = \| -(\partial^2\Phi/\partial Y_A\partial Y_B)_0 \|$ introduced in Sec. 57 defines the thermodynamic potential in the first approximation

$$\Phi = \Phi_0 - \frac{1}{2} M_{AB} Y_A Y_B \qquad (60.8)$$

and the dependence of thermodynamic coordinates on thermodynamic forces

$$y_A = M_{AB} Y_B. \qquad (60.9)$$

The matrix of internal energy $\| N_{AB} \| = \|(\partial^2 U/\partial y_A\partial y_B)_0 \|$ plays a similar role:

$$U = U_0 + \frac{1}{2} N_{AB} y_A y_B, \qquad (60.10)$$

$$Y_A = N_{AB} y_B. \qquad (60.11)$$

It is evidently the reciprocal of the matrix of a thermodynamic potential: $N = M^{-1}$; in this and only in this case E is simply a unit matrix.

In more detailed notation (60.11) becomes*

$$\Theta = (T_0/C_v)\,\Sigma - (T_0/C_v)\,q_k\widetilde{D}_k - (T_0/C_v)\,\beta_\mu\varepsilon_\mu, \qquad (60.12a)$$

$$E_i = -(T_0/C_v)\,q_i\Sigma + 4\pi\eta_{ik}\widetilde{D}_k - h_{i\mu}\varepsilon_\mu, \qquad (60.12b)$$

$$\sigma_\lambda = -(T_0/C_v)\,\beta_\lambda\Sigma - h_{k\lambda}\widetilde{D}_k + c_{\lambda\mu}\varepsilon_\mu. \qquad (60.12c)$$

Here C_v is heat capacity per unit volume at constant strains and constant induction, η_{ik} is adiabatic dielectric impermeability at

* Letters *a*, *b*, *c* in the numbers of formulas refer to the thermal, electrical and mechanical quantities respectively.

constant strains, $c_{\lambda\mu}$ are adiabatic elasticity coefficients at constant induction, β_λ are thermoelastic coefficients at constant induction, q_i and $h_{i\mu}$ are the vector and tensor specifying pyroelectric and piezoelectric properties of a crystal and having no conventional names (the name "Mason's constant" for $h_{i\mu}$ has not apparently become widely used).

As a second example we shall consider potential $H_{\mathrm{el}}(S, \boldsymbol{E}, \boldsymbol{\varepsilon})$. From (60.3), we obtain

$$\Theta = \left(\frac{\partial^2 H_{\mathrm{el}}}{\partial S^2}\right)_0 \Sigma + \left(\frac{\partial^2 H_{\mathrm{el}}}{\partial S \partial \boldsymbol{E}}\right)_0 \cdot \boldsymbol{E} + \left(\frac{\partial^2 H_{\mathrm{el}}}{\partial S \partial \boldsymbol{\varepsilon}}\right)_0 : \boldsymbol{\varepsilon}, \quad (60.13a)$$

$$\tilde{\boldsymbol{D}} = -\left(\frac{\partial^2 H_{\mathrm{el}}}{\partial \boldsymbol{E} \partial S}\right)_0 \Sigma - \left(\frac{\partial^2 H_{\mathrm{el}}}{\partial \boldsymbol{E} \partial \boldsymbol{E}}\right)_0 \cdot \boldsymbol{E} - \left(\frac{\partial^2 H_{\mathrm{el}}}{\partial \boldsymbol{E} \partial \boldsymbol{\varepsilon}}\right)_0 : \boldsymbol{\varepsilon}, \quad (60.13b)$$

$$\boldsymbol{\sigma} = \left(\frac{\partial^2 H_{\mathrm{el}}}{\partial \boldsymbol{\varepsilon} \partial S}\right)_0 \Sigma + \left(\frac{\partial^2 H_{\mathrm{el}}}{\partial \boldsymbol{\varepsilon} \partial \boldsymbol{E}}\right)_0 \cdot \boldsymbol{E} + \left(\frac{\partial^2 H_{\mathrm{el}}}{\partial \boldsymbol{\varepsilon} \partial \boldsymbol{\varepsilon}}\right)_0 : \boldsymbol{\varepsilon}, \quad (60.13c)$$

or in a matrix form

$$\left\| \begin{matrix} \Theta \\ -\tilde{\boldsymbol{D}} \\ \boldsymbol{\sigma} \end{matrix} \right\| = \left\| \begin{matrix} (\partial^2 H_{\mathrm{el}}/\partial S^2)_0 & (\partial^2 H_{\mathrm{el}}/\partial S\, \partial \boldsymbol{E})_0 & (\partial^2 H_{\mathrm{el}}/\partial S\, \partial \boldsymbol{\varepsilon})_0 \\ (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{E}\, \partial S)_0 & (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{E}\, \partial \boldsymbol{E})_0 & (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{E}\, \partial \boldsymbol{\varepsilon})_0 \\ (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{\varepsilon}\, \partial S)_0 & (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{\varepsilon}\, \partial \boldsymbol{E})_0 & (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{\varepsilon}\, \partial \boldsymbol{\varepsilon})_0 \end{matrix} \right\| \left\| \begin{matrix} \Sigma \\ \cdot \boldsymbol{E} \\ : \boldsymbol{\varepsilon} \end{matrix} \right\|. \quad (60.13)$$

The potential with respect to the supplementary set of arguments is $\Phi_{\mathrm{mech}}(T, \tilde{\boldsymbol{D}}, \boldsymbol{\sigma})$; the equation for its matrix, similar to (60.13), is as follows:

$$\left\| \begin{matrix} \Sigma \\ -\boldsymbol{E} \\ \boldsymbol{\varepsilon} \end{matrix} \right\| = \left\| \begin{matrix} -(\partial^2 \Phi_{\mathrm{mech}}/\partial T^2)_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial T\, \partial \tilde{\boldsymbol{D}})_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial T\, \partial \boldsymbol{\sigma})_0 \\ -(\partial^2 \Phi_{\mathrm{mech}}/\partial \tilde{\boldsymbol{D}}\, \partial T)_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial \tilde{\boldsymbol{D}}\, \partial \tilde{\boldsymbol{D}})_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial \tilde{\boldsymbol{D}}\, \partial \boldsymbol{\sigma})_0 \\ -(\partial^2 \Phi_{\mathrm{mech}}/\partial \boldsymbol{\sigma}\, \partial T)_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial \boldsymbol{\sigma}\, \partial \tilde{\boldsymbol{D}})_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial \boldsymbol{\sigma}\, \partial \boldsymbol{\sigma})_0 \end{matrix} \right\| \left\| \begin{matrix} \Theta \\ \cdot \tilde{\boldsymbol{D}} \\ : \boldsymbol{\sigma} \end{matrix} \right\|. \quad (60.14)$$

Comparing (60.13) and (60.14) we see that the matrices of potentials H_{el} and Φ_{mech}, in full agreement with (60.7) are connected by relation

$$\left\| \begin{matrix} -(\partial^2 \Phi_{\mathrm{mech}}/\partial T^2)_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial T\, \partial \tilde{\boldsymbol{D}})_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial T\, \partial \boldsymbol{\sigma})_0 \\ -(\partial^2 \Phi_{\mathrm{mech}}/\partial \tilde{\boldsymbol{D}}\, \partial T)_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial \tilde{\boldsymbol{D}}\, \partial \tilde{\boldsymbol{D}})_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial \tilde{\boldsymbol{D}}\, \partial \boldsymbol{\sigma})_0 \\ -(\partial^2 \Phi_{\mathrm{mech}}/\partial \boldsymbol{\sigma}\, \partial T)_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial \boldsymbol{\sigma}\, \partial \tilde{\boldsymbol{D}})_0 & -(\partial^2 \Phi_{\mathrm{mech}}/\partial \boldsymbol{\sigma}\, \partial \boldsymbol{\sigma})_0 \end{matrix} \right\|^{-1} =$$

$$= \left\| \begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix} \right\| \left\| \begin{matrix} (\partial^2 H_{\mathrm{el}}/\partial S^2)_0 & (\partial^2 H_{\mathrm{el}}/\partial S\, \partial \boldsymbol{E})_0 & (\partial^2 H_{\mathrm{el}}/\partial S\, \partial \boldsymbol{\varepsilon})_0 \\ (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{E}\, \partial S)_0 & (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{E}\, \partial \boldsymbol{E})_0 & (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{E}\, \partial \boldsymbol{\varepsilon})_0 \\ (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{\varepsilon}\, \partial S)_0 & (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{\varepsilon}\, \partial \boldsymbol{E})_0 & (\partial^2 H_{\mathrm{el}}/\partial \boldsymbol{\varepsilon}\, \partial \boldsymbol{\varepsilon})_0 \end{matrix} \right\| \left\| \begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix} \right\|. \quad (60.15)$$

The matrix elements in (60.13)-(60.15) are not only numbers, but also vectors and tensors; for instance, two unities of three in matrices E (60.15) are tensors.

Sec. 61. Dependence of Thermodynamic Coefficients on Conditions of Measurement

Coefficients characterizing the properties of substances depend—sometimes quite considerably—on the conditions under which they are measured: heat capacity measured at constant volume is not equal to heat capacity measured at constant pressure; adiabatic compressibility is not equal to isothermal compressibility. Crystals are no exception from this general rule; thus, the mechanical properpties of crystals depend on the electrical conditions (conducting or non-conducting are the piezoelectric slab plates), while the electrical conditions depend on the mechanical ones (is the slab capable of free straining or it is clamped mechanically).

Every thermodynamic potential generates its thermodynamic matrix and, correspondingly, its system of thermodynamic coefficients which serve as the elements of this matrix.

We shall start from a system of thermodynamic coefficients generated by the thermodynamic potential Φ, i.e. the system defined by the equations*

$$\Sigma = \frac{C_p}{T_0}\Theta + p_k E_k + \alpha_\mu \sigma_\mu, \tag{61.1a}$$

$$\widetilde{D}_i = p_i \Theta + \frac{1}{4\pi}\varkappa_{ik} E_k + d_{i\mu}\sigma_\mu, \tag{61.1b}$$

$$\varepsilon_\lambda = \alpha_\lambda \Theta + d_{k\lambda} E_k + s_{\lambda\mu}\sigma_\mu. \tag{61.1c}$$

Coefficients $\varkappa_{ik}$, $s_{\lambda\mu}$, $d_{i\mu}$ are measured at constant temperature. Let us calculate the values of these coefficients when they are measured not under isothermal, but under adiabatic conditions.

In an adiabatic process the entropy is constant, while the temperature varies. Its variations can easily be determined from equation (61.1a):

$$\Theta = \frac{T_0}{C_p}\Sigma - \frac{T_0}{C_p} p_k E_k - \frac{T_0}{C_p}\alpha_\mu \sigma_\mu \tag{61.2a}$$

(for the sake of generality we do not assume that $\Sigma = 0$, bearing in mind that the entropy can be kept constant, but not equal to S_0). Let us substitute the obtained value Θ into (61.1b) and (61.1c):

$$\widetilde{D}_i = \frac{T_0}{C_p} p_i \Sigma + \left(\frac{1}{4\pi}\varkappa_{ik} - \frac{T_0}{C_p} p_i p_k\right) E_k + \left(d_{i\mu} - \frac{T_0}{C_p} p_i \alpha_\mu\right)\sigma_\mu, \tag{61.2b}$$

$$\varepsilon_\lambda = \frac{T_0}{C_p}\alpha_\lambda \Sigma + \left(d_{k\lambda} - \frac{T_0}{C_p} p_k \alpha_\lambda\right) E_k + \left(s_{\lambda\mu} - \frac{T_0}{C_p}\alpha_\lambda \alpha_\mu\right)\sigma_\mu. \tag{61.2c}$$

* See footnote on page 409.

Whence we obtain the adiabatic values of the coefficients

$$\varkappa_{ik}^{(S)} = \varkappa_{ik} - \frac{4\pi T_0}{C_p} p_i p_k, \quad s_{\lambda\mu}^{(S)} = s_{\lambda\mu} - \frac{T_0}{C_p} \alpha_\lambda \alpha_\mu, \quad d_{i\mu}^{(S)} = d_{i\mu} - \frac{T_0}{C_p} p_i \alpha_\mu. \tag{61.3}$$

Thus the adiabatic dielectric permittivities and piezoelectric coefficients differ from the isothermal ones only in pyroelectric crystals. Even though some adiabatic coefficients of elastic compliance differ from the corresponding isothermal coefficients practically in all solids, in crystals of sufficiently high symmetry some adiabatic coefficients coincide with the isothermal ones (for instance, in cubic crystals $s_{44}^{(S)} = s_{44}$). Formulas (61.3) also show that diagonal adiabatic coefficients of dielectric permittivity ($\varkappa_{11}$, $\varkappa_{22}$, $\varkappa_{33}$) and elastic compliance (s_{11}, s_{22}, . . ., s_{66}) are no larger than the corresponding isothermal ones; this statement, as well as other thermodynamic inequalities, are valid in an arbitrary system of coordinates.

Equations (61.2) determine in essence the thermodynamic matrix for enthalpy $H = \Phi + TS$ which is a thermodynamic potential with respect to variables S, $\boldsymbol{E}$, $\boldsymbol{\sigma}$. Moreover, the elements of this matrix are expressed in terms of quantities readily measured in experiment, i.e. the elements of matrix M.

Evidently, the same can always be done on substituting one independent variable. Let us now consider the case when not one but three independent variables are substituted at once: we shall calculate the coefficients C_p, $s_{\lambda\mu}$ and α_λ not at constant electric field as in (61.1) but at constant induction. For this purpose we shall solve the system of equations (61.1b) with respect to the components of vector $\boldsymbol{E}$. First, we compute tensor $\boldsymbol{\eta}^* = \boldsymbol{\varkappa}^{-1}$, i.e. the tensor of dielectric impermeability measured in an isothermal process and at constant voltages. With the aid of this tensor we find

$$E_k = -4\pi\eta_{kl}^* p_l \Theta + 4\pi\eta_{kl}^* \widetilde{D}_l - 4\pi\eta_{kl}^* d_{l\mu}\sigma_\mu, \tag{61.4b}$$

and next, substituting this expression into (61.1a) and (61.1c) we obtain

$$\Sigma = (C_p/T - 4\pi\eta_{kl}^* p_k p_l)\,\Theta + 4\pi\eta_{kl}^* p_k \widetilde{D}_l + (\alpha_\mu - 4\pi\eta_{kl}^* p_k\, d_{l\mu})\,\sigma_\mu, \tag{61.4a}$$

$$\varepsilon_\lambda = (\alpha_\lambda - 4\pi\eta_{kl}^* p_l\, d_{k\lambda})\,\Theta + 4\pi\eta_{kl}^*\, d_{k\lambda}\widetilde{D}_l + (s_{\lambda\mu} - 4\pi\eta_{kl}^*\, d_{k\lambda}\, d_{l\mu})\,\sigma_\mu. \tag{61.4c}$$

The equations (61.4) determine the matrix corresponding to the thermodynamic potential $\Phi_{\text{mech}} = \Phi + \boldsymbol{E}\cdot\widetilde{\boldsymbol{D}}$. It can be seen that the thermodynamic coefficients at constant induction differ from similar coefficients at a constant electric field only in pyroelectric (C_p and α_λ) and piezoelectric ($s_{\lambda\mu}$) crystals.

In the transition from the isothermal coefficients to the adiabatic ones and from the coefficients measured at constant field to coefficients measured at constant induction there arises the need for corrections whose calculation shows that for an overwhelming majority of crystals* they are extremely small, of the order of 1% at most. Pyroelectric coefficients measured under constant strain and constant voltage are an exception: the difference between them is of the same order as that of the coefficients themselves. To find this difference, we must calculate the coefficients $c^*_{\lambda\mu}$, i.e. the elasticity coefficients for an isothermal process at constant electric field, from the equation $s_{\lambda\mu}c^*_{\mu\nu}=\delta_{\lambda\nu}$. Having solved (61.1c) with respect to σ_μ, with the aid of these coefficients, we find

$$\sigma_\mu = -c^*_{\mu\nu}\alpha_\nu\Theta - c^*_{\mu\nu}\, d_{k\nu}E_k + c^*_{\mu\nu}\varepsilon_\nu, \tag{61.5c}$$

and substituting σ_μ into (61.1a) and (61.1b), we have

$$\Sigma = \left(\frac{C_p}{T} - c^*_{\mu\nu}\alpha_\mu\alpha_\nu\right)\Theta + (p_k - c^*_{\mu\nu}\alpha_\mu\, d_{k\nu})\, E_k + c^*_{\mu\nu}\alpha_\mu\varepsilon_\nu, \tag{61.5a}$$

$$\widetilde{D}_i = (p_i - d_{i\mu}c^*_{\mu\nu}\alpha_\nu)\,\Theta + (\widetilde{\varkappa}_{ik} - d_{i\mu}c^*_{\mu\nu}\, d_{k\nu})\, E_k + d_{i\mu}c^*_{\mu\nu}\varepsilon_\nu. \tag{61.5b}$$

Thus, under constant strain, the pyroelectric coefficients are

$$p_i^{(\varepsilon)} = p_i - d_{i\mu}c^*_{\mu\nu}\alpha_\nu. \tag{61.6}$$

In all pyroelectric crystals the pyroelectric coefficients measured under constant voltage differ to some degree from those measured under constant strain, since all the pyroelectric crystals are at the same time piezoelectric crystals.

Under ordinary conditions of a physical experiment and technological use of crystals it is not feasible, as a rule, to act on a crystal by all conceivable thermodynamic forces. If, for example, a crystal is used as a dielectric slab in a plane-parallel capacitor, the electric field strength in it is perpendicular to the plane of the slab. The load set-ups, in turn, usually allow obtaining only some particular kinds of stress; as applied to the slab, these can be, for instance, compression and tension stresses directed along the normal $\boldsymbol{n}$ to the plane of the slab, or in some definite direction $\boldsymbol{q}$ perpendicular to this normal ($\boldsymbol{n}$ and $\boldsymbol{q}$ are unit vectors). Under these conditions the thermodynamic potential of the crystal depends in essence on only three variables (T, $\boldsymbol{E}$, $\boldsymbol{\sigma}$) and not on ten as in a general case. It is clear that in this case all the other thermodynamic potentials must be also determined by three corresponding independent variables, although generally all the components of the induction vector and the strain tensor differ from zero. The point is that only one component of the induction vector ($\widetilde{\boldsymbol{D}}\cdot\boldsymbol{n}$) and one component of the strain tensor ($\boldsymbol{n}\cdot\boldsymbol{\varepsilon}\cdot\boldsymbol{n}$ or $\boldsymbol{q}\cdot\boldsymbol{\varepsilon}\cdot\boldsymbol{q}$)

* This does not relate to the ferroelectric crystals.

are important, all the others are unambiguously determined by them (if temperature or entropy is known).

Let us consider now, for example, the pyroelectric effect in a crystal slab cut so that the pyroelectric coefficients vector is perpendicular to the slab plane, i.e. $\boldsymbol{p} = p\boldsymbol{n}$. If the plates are closed and no stresses are applied to the slab, the generalized thermodynamic coordinates will be

$$\Sigma = (C_p/T_0)\,\Theta, \tag{61.7a}$$

$$\boldsymbol{n} : \widetilde{\boldsymbol{D}} = p\Theta, \tag{61.7b}$$

$$\boldsymbol{nn} : \boldsymbol{\varepsilon} = (\boldsymbol{nn} : \boldsymbol{\alpha})\,\Theta. \tag{61.7c}$$

The charge density on the plate is

$$\rho_{\text{surf}} = \boldsymbol{n}\cdot\widetilde{\boldsymbol{D}} = p\Theta, \tag{61.8}$$

whence the pyroelectric coefficient p is determined at constant (zero) stresses.

Now let us apply a compressive stress $\boldsymbol{\sigma} = \sigma\boldsymbol{nn}$ such that the slab thickness would not change with the temperature rise. The electric field in the slab is still zero, so that

$$\Sigma = (C_p/T_0)\,\Theta + (\boldsymbol{\alpha} : \boldsymbol{nn})\,\sigma, \tag{61.9a}$$

$$\boldsymbol{n}\cdot\widetilde{\boldsymbol{D}} = p\Theta + (\boldsymbol{n}\cdot\mathbf{d} : \boldsymbol{nn})\,\sigma, \tag{61.9b}$$

$$\boldsymbol{nn} : \boldsymbol{\varepsilon} = (\boldsymbol{nn} : \boldsymbol{\alpha})\,\Theta + (\boldsymbol{nn} : \mathbf{s} : \boldsymbol{nn})\,\sigma. \tag{61.9c}$$

Since the thickness of the plate remains unchanged, $\boldsymbol{nn} : \boldsymbol{\varepsilon} = 0$, and from (61.9c), we find

$$\sigma = -\frac{\boldsymbol{nn} : \boldsymbol{\alpha}}{\boldsymbol{nn} : \mathbf{s} : \boldsymbol{nn}}\,\Theta, \tag{61.10c}$$

and substituting σ into (61.9a) and (61.9b), we obtain two more equations

$$\Sigma = \left[\frac{C_p}{T_0} - \frac{(\boldsymbol{nn} : \boldsymbol{\alpha})^2}{\boldsymbol{nn} : \mathbf{s} : \boldsymbol{nn}}\right]\Theta, \tag{61.10a}$$

$$\boldsymbol{n}\cdot\widetilde{\boldsymbol{D}} = \left[p - \frac{(\boldsymbol{nn} : \boldsymbol{\alpha})\,(\boldsymbol{n}\cdot\mathbf{d} : \boldsymbol{nn})}{\boldsymbol{nn} : \mathbf{s} : \boldsymbol{nn}}\right]\Theta. \tag{61.10b}$$

Evidently, under these conditions the role of the pyroelectric coefficient is played by the coefficient of Θ in (61.10b); it should naturally be denoted by $p_{(\boldsymbol{nn}:\boldsymbol{\varepsilon})}$. We should emphasize that this is not the pyroelectric coefficient at constant strains: constant are the component of the strain tensor $\boldsymbol{nn} : \boldsymbol{\varepsilon}$ and all the components of the stress tensor differing from $\boldsymbol{nn} : \boldsymbol{\sigma}$.

Other experiments of the same nature are considered similarly. Great care is always to be taken, as in the above example, to know what particular components of vectors $\boldsymbol{E}$ and $\widetilde{\boldsymbol{D}}$ and tensors $\boldsymbol{\sigma}$ and $\boldsymbol{\varepsilon}$ remain constant under conditions of the experiment.

Now let us calculate the elements of the electric enthalpy matrix H_{el}; they will be required in Sec. 62 for computing the piezoelectric corrections to the velocities of propagation of elastic waves in crystals. Since the elements of the enthalpy matrix H have already been found (see (61.2)), we shall proceed from the definition $H_{el} = H + \sigma_\lambda \varepsilon_\lambda$. Therefore we should begin with the calculation of a matrix reciprocal of $s_{\lambda\mu}^{(S)}$ (see (61.3)), i.e. with the solution of a system of equations

$$[s_{\lambda\mu} - (T_0/C_p)\,\alpha_\lambda \alpha_\mu]\, c_{\mu\varkappa}^{(E)} = \delta_{\lambda\varkappa} \tag{61.11}$$

with respect to $c_{\mu\varkappa}^{(E)}$, i.e. the adiabatic coefficients of elasticity at constant electric field strength. This makes it possible to solve (61.2c) with respect to σ_λ:

$$\sigma_\lambda = -(T_0/C_p)\, c_{\lambda\mu}^{(E)} \alpha_\mu \Sigma - c_{\lambda\mu}^{(E)} d_{k\mu}^{(S)} E_k + c_{\lambda\mu}^{(E)} \varepsilon_\mu. \tag{61.12c}$$

The coefficients of Σ, E_k, ε_μ form six lower rows of the matrix of electric enthalpy. We shall find the other matrix elements by substituting (61.12c) in (61.2a) and (61.2b) and collecting the coefficients of Σ, E_k and ε_λ:

$$\Theta = (T_0/C_p)\,[1 + (T_0/C_p)\,\alpha_\lambda c_{\lambda\mu}^{(E)} \alpha_\mu]\,\Sigma - \\ - (T_0/C_p)\,(p_k - \alpha_\lambda c_{\lambda\mu}^{(E)} d_{k\mu}^{(S)})\, E_k - (T_0/C_p)\,\alpha_\lambda c_{\lambda\mu}^{(E)} \varepsilon_\mu, \tag{61.12a}$$

$$\tilde{D}_i = (T_0/C_p)\,(p_i - d_{i\lambda}^{(S)} c_{\lambda\mu}^{(E)} \alpha_\mu)\,\Sigma + \\ + (\tilde{\varkappa}_{ik}^{(S)} - d_{i\lambda}^{(S)} c_{\lambda\mu}^{(E)} d_{k\mu}^{(S)})\, E_k + d_{i\lambda}^{(S)} c_{\lambda\mu}^{(E)} \varepsilon_\mu. \tag{61.12b}$$

These are the coefficients that form the four upper rows of the matrix sought for; it is only necessary to multiply by -1 the rows corresponding to vector $\tilde{D}$ (see (60.13)).

For the adiabatic process $\Sigma = 0$ and expressions (61.12b, c) can be represented as

$$\begin{aligned} \tilde{D}_i &= \tilde{\varkappa}_{ik}^{(S,\,\varepsilon)} E_k + e_{i\mu} \varepsilon_\mu, \\ \sigma_\lambda &= -e_{k\lambda} E_k + c_{\lambda\mu}^{(E)} \varepsilon_\mu; \end{aligned} \tag{61.13}$$

the introduced thermodynamic coefficients are connected with the second derivatives of the thermodynamic potential by relations (61.11) and

$$\tilde{\varkappa}_{ik}^{(S,\,\varepsilon)} = \varkappa_{ik} - d_{i\lambda} c_{\lambda\mu}^{(E)} d_{k\mu} - (T_0/C_p)\, p_i p_k + (T_0/C_p) \times \\ \times (p_i \alpha_\lambda c_{\lambda\mu}^{(E)} d_{k\mu} + d_{i\lambda} c_{\lambda\mu}^{(E)} \alpha_\mu p_k) - (T_0/C_p)^2\, p_i \alpha_\lambda c_{\lambda\mu}^{(E)} \alpha_\mu p_k, \tag{61.14}$$

$$e_{i\mu} = [d_{i\lambda} - (T_0/C_p)\, p_i \alpha_\lambda]\, c_{\lambda\mu}^{(E)}. \tag{61.15}$$

The examples considered show that the experimental determination of the elements of any one of thermodynamic matrices makes it

possible to compute the elements of all the other thermodynamic matrices. Thus, having computed the tensor $\eta = [\varkappa^{(S,\varepsilon)}]^{-1}$ where $\varkappa^{(S,\varepsilon)}$ is the set of the coefficients of $\boldsymbol{E}$ in (61.1b), $\boldsymbol{E}$ is expressible as a function of Σ, $\tilde{\boldsymbol{D}}$, and ε, and upon the substitution of the found value of $\boldsymbol{E}$ in (61.1a) and (61.1c) $\boldsymbol{\Theta}$ and σ can be expressed as functions of Σ, $\tilde{\boldsymbol{D}}$, and ε. A comparison of the obtained relations with (60.12) permits expressing the thermodynamic coefficients T_0/C_v, η_{ik}, $c_{\lambda\mu}$, β_λ, q_i, and $h_{i\mu}$, which are the second derivatives of the internal energy, in terms of the thermodynamic potential second derivatives C_p/T_0, $\varkappa_{ik}$, $s_{\lambda\mu}$, p_i, α_λ, $d_{i\mu}$. In actual practice, however, it is not so simple as this. The accuracy of the experimental data is limited. The accuracy diminishes essentially when the elements of the first thermodynamic matrix are calculated from the experimental data, and it diminishes still further in succeeding calculations. Therefore careful estimation of the accuracy of the obtained results is necessary when such calculations are made. To reduce the errors it is advantageous to start from redundant experimental data rather than from a necessary minimum. The computations in this case of course become more complicated, but their results become more reliable. The methods of such calculations, meant specially for crystal-physical computations, were described by J. F. Nye (1957).

Sec. 62. Elastic Waves in Piezoelectric Crystals

To investigate the peculiarities of the propagation of elastic waves in piezoelectric crystals it is necessary to consider the solutions of an interconnected set of equations of elastodynamics and electrostatics. Using the equations of electrostatics instead of those of electrodynamics we certainly commit an error; by the order of its magnitude it is equal to the square of the ratio of the sound velocity in a crystal to the light velocity i.e. it is quite negligible.

The set which we have to solve is this:

$$\operatorname{Div} \sigma = \rho \ddot{\boldsymbol{u}}, \tag{62.1}$$

$$\operatorname{div} \boldsymbol{D} = 0. \tag{62.2}$$

Equations curl $\boldsymbol{E} = 0$ and Inc $\varepsilon = 0$ can be satisfied identically, if the stress tensor σ and the electric induction vector $\boldsymbol{D}$ are expressed in terms of the potential φ and displacement vector $\boldsymbol{u}$. For this it is necessary to use the matrix of such a thermodynamic potential which is a function of the vector of electric field strength $\boldsymbol{E} = -\operatorname{grad} \varphi$, of the strain tensor $\varepsilon = \operatorname{Def} \boldsymbol{u}$ and, finally, the entropy S, because the propagation of elastic waves is an adiabatic process. Such is the thermodynamic potential $H_{\text{el}} = U - \boldsymbol{E}\cdot\tilde{\boldsymbol{D}}$, which was considered

in detail in Sec. 61. The formulas derived there (61.13) can be conveniently represented in the form*

$$D_i = -\varkappa_{ik}^{(S,\,\varepsilon)} \frac{\partial \varphi}{\partial x_k} + 4\pi e_{ikl} \frac{\partial u_k}{\partial x_l}, \tag{62.3}$$

$$\sigma_{ij} = e_{kij} \frac{\partial \varphi}{\partial x_k} + c_{ijkl}^{(E)} \frac{\partial u_k}{\partial x_l}. \tag{62.4}$$

Here tensor $\varepsilon = \operatorname{Def} \boldsymbol{u}$ is replaced by tensor $\partial \boldsymbol{u}/\partial \boldsymbol{r}$ because when multiplied by tensors $\mathbf{c}$ and $\mathbf{e}$ symmetric with respect to the last two indices, they both give identical results. The components e_{ikl} of tensor $\mathbf{e}$ are connected with the coefficients $e_{i\mu}$ by the relations (see Appendix F)

$$e_{i\mu} = e_{ikl} \quad (kl \leftrightarrow \mu = 1, \ldots, 6).$$

Substituting expressions (62.4) and (62.3) in equations (62.1) and (62.2) respectively, we obtain a system of partial differential equations of the second order with respect to functions $u_i(\boldsymbol{r}, t)$ and $\varphi(\boldsymbol{r}, t)$:

$$c_{ijkl} \frac{\partial^2 u_k}{\partial x_i \partial x_l} + e_{kij} \frac{\partial^2 \varphi}{\partial x_k \partial x_i} = \rho \frac{\partial^2 u_j}{\partial t^2}, \tag{62.5}$$

$$-\varkappa_{ik} \frac{\partial^2 \varphi}{\partial x_i \partial x_k} + 4\pi e_{ik} \frac{\partial^2 u_k}{\partial x_i \partial x_l} = 0. \tag{62.6}$$

Using the notation given in Sec. 56 and denoting by $A\xi$ the amplitude of the potential we write down the plane waves of the displacement and the potential rigidly related to each other:

$$\boldsymbol{u} = A\boldsymbol{p} \exp\left[(2\pi i/\lambda)(\boldsymbol{m}\cdot\boldsymbol{r} - vt)\right],$$

$$\varphi = A\xi \exp\left[(2\pi i/\lambda)(\boldsymbol{m}\cdot\boldsymbol{r} - vt)\right].$$

Substituting them in equations (62.5) and (62.6), we have

$$M_{jk}p_k + \xi g_j = \rho v^2 p_j, \qquad \mathbf{M}\cdot\boldsymbol{p} + \xi \boldsymbol{g} = \rho v^2 \boldsymbol{p}; \tag{62.7}$$

$$-\xi K + 4\pi g_k p_k = 0, \qquad -\xi K + 4\pi \boldsymbol{g}\cdot\boldsymbol{p} = 0, \tag{62.8}$$

which contain the notation

$$M_{jk} = e_{ijkl} m_i m_l, \qquad \mathbf{M} = \boldsymbol{m}\cdot\mathbf{c}\cdot\boldsymbol{m};$$

$$g_k = e_{ikl} m_i m_l, \qquad \boldsymbol{g} = \boldsymbol{m}\cdot\mathbf{e}\cdot\boldsymbol{m};$$

$$K = \varkappa_{il} m_i m_l, \qquad K = \boldsymbol{m}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{m}.$$

Thus, along with the Christoffel tensor $\mathbf{M}$ (see Sec. 56) we introduce the vector $\mathbf{g}$ and the scalar K analogous to it. From (62.8), we find

$$\xi = \frac{4\pi}{K} g_k p_k = \frac{4\pi}{K} \boldsymbol{g}\cdot\boldsymbol{p}$$

* Subsequently we shall write $\varkappa_{ik}$ and c_{ijkl} instead of $\varkappa_{ik}^{(S,\,\varepsilon)}$ and $c_{ijkl}^{(E)}$ respectively.

and, substituting it in (62.7), we obtain

$$\left(M_{jk}+\frac{4\pi}{K}g_jg_k\right)p_k=\rho v^2p_j,\quad \left(\mathbf{M}+\frac{4\pi}{K}\,\boldsymbol{gg}\right)\cdot\boldsymbol{p}=\rho v^2\boldsymbol{p}. \qquad (62.9)$$

This system of equations can be naturally called the Christoffel set of equations for piezoelectric crystals. Thus the entire difference between our case and that of elastic waves in a non-piezoelectric crystal consists in the replacement of the usual Christoffel tensor $\mathbf{M}$ by the tensor $\mathbf{M}+(4\pi/K)\boldsymbol{gg}$.

Let us consider, for example, the propagation of elastic waves in a crystal of class 2 along a 2-fold axis X_2. The calculation of the components of tensor $\mathbf{M}$ is greatly facilitated in this case because $M_{jk}=c_{2jk2}$. Hence (see Table E.18),

$$M_{11}=c_{66},\qquad M_{22}=c_{22},\qquad M_{33}=c_{44},$$
$$M_{23}=0,\qquad M_{31}=c_{46},\qquad M_{12}=0.$$

The components of vector $\boldsymbol{g}$ in this case are $g_j=e_{2j2}$. According to the Table E.11

$$g_1=0,\quad g_2=e_{22},\quad g_3=0.$$

Finally, $K=\varkappa_{22}$. The Christoffel equations (62.9) now appear as

$$c_{66}p_1+c_{46}p_3=\rho v^2p_1,$$
$$(c_{22}+4\pi e_{22}^2/\varkappa_{22})\,p_2=\rho v^2p_2,$$
$$c_{46}p_1+c_{44}p_3=\rho v^2p_3.$$

It is evident that in this case only the velocity of the longitudinal waves changes becoming

$$v=\sqrt{\frac{1}{\rho}\left(c_{22}+\frac{4\pi e_{22}^2}{\varkappa_{22}}\right)}\approx v_0\left(1+\frac{1}{2}\frac{4\pi e_{22}^2}{\varkappa_{22}c_{22}}\right),$$

where v_0 is the velocity calculated without account taken of the piezoelectric effect. The ratio $4\pi e^2{}_{22}/(\varkappa_{22}c_{22})$ plays the role of the square of the electromechanical coupling coefficient.

As a second, somewhat more complicated example we shall consider the propagation of elastic waves in a crystal of class m in the direction of the perpendicular to the symmetry plane; this is again the axis X_2. The tensor $\mathbf{M}$ and the scalar K were already found in the preceding example. The components of vector $\boldsymbol{g}$ are still equal to $g_j=e_{2j2}$, but now from Table E.11, we find

$$g_1=e_{26},\quad g_2=0,\quad g_3=e_{24}.$$

Therefore Christoffel's equations take the form

$$\left(c_{66}+\frac{4\pi e_{26}^2}{\varkappa_{22}}\right)p_1+\left(c_{46}+\frac{4\pi e_{26}e_{24}}{\varkappa_{22}}\right)p_3=\rho v^2p_1,$$
$$c_{22}p_2=\rho v^2p_2,$$
$$\left(c_{46}+\frac{4\pi e_{26}e_{24}}{\varkappa_{22}}\right)p_1+\left(c_{44}+\frac{4\pi e_{24}^2}{\varkappa_{22}}\right)p_3=\rho v^2p_3.$$

Clearly, in this case the piezoelectric correction to the velocity of longitudinal waves is zero, but the velocities and polarization directions of transversal waves are changed.

It was shown recently that in non-centrosymmetric crystals the influence of an electric field can result in both linear and non-linear changes of the phase velocities of elastic waves (Blistanov, Petrakov, Shaskolskaya, et al. 1977).

Sec. 63. Thermodynamic Inequalities

In the course of an irreversible process the entropy of a body changes not only as a result of its transfer from the surrounding bodies to the given one and vice versa, but also because the entropy develops in the body itself. This fact is expressed by an inequality

$$\frac{dS}{dt}-\frac{1}{T}\frac{dQ}{dt}\geqslant 0 \tag{63.1}$$

which is one of the possible formulations of the second law of thermodynamics. On the other hand, according to the first law of thermodynamics, the rate of heat supply is

$$\frac{dQ}{dt}=\frac{dU}{dt}-E\cdot\frac{d\widetilde{D}}{dt}-\sigma:\frac{d\varepsilon}{dt}. \tag{63.2}$$

Bearing in mind the positiveness of the absolute temperature T, we obtain from (63.1) and (63.2) an inequality

$$\frac{dU}{dt}-T\frac{dS}{dt}-E\cdot\frac{d\widetilde{D}}{dt}-\sigma:\frac{d\varepsilon}{dt}=\frac{dU}{dt}-X_A\frac{dx_A}{dt}\leqslant 0. \tag{63.3}$$

If the system is not in a state of thermodynamic equilibrium, the thermodynamic potential $\Phi = U - X_A x_A$ depends not only on generalized thermodynamic forces X_A but also on other arguments, so that the rate of its variation at constant thermodynamic forces is

$$\left(\frac{d\Phi}{dt}\right)_X=\frac{d}{dt}(U-X_A x_A)_X=\frac{dU}{dt}-X_A\frac{dx_A}{dt}. \tag{63.4}$$

Comparing this with (63.3), we have

$$\left(\frac{d\Phi}{dt}\right)_X\leqslant 0 \tag{63.5}$$

—at constant thermodynamic forces the thermodynamic potential Φ of a system not in equilibrium decreases, and that of an equilibrium system remains unchanged. In other words, the state of thermodynamic equilibrium differs from all other states of a substance characterized by the same thermodynamic forces, by the fact that the thermodynamic potential attains its minimum value in the state of equilibrium, and any possible deviations from this value must be positive:

$$(\delta\Phi)_X>0. \tag{63.6}$$

When the thermodynamic potential of the equilibrium state is compared with that of close non-equilibrium states, it must be borne in mind that non-equilibrium states are not only determined by 10 generalized forces, but also depend on other parameters. If generalized coordinates are the parameters, then

$$(\delta\Phi)_X = \delta\,(U - X_A x_A)_X = \frac{dU}{\partial x_A}\,\delta x_A + \frac{1}{2}\,\frac{\partial^2 U}{\partial x_A \partial x_B}\,\delta x_A \delta x_B - X_A \delta x_A.$$

Function U is expanded in a series up to the second-order terms, since the first-order terms are mutually cancelled: $\frac{\partial U}{\partial x_A} - X_A = 0$. Thus an inequality follows from (63.6)

$$\frac{\partial^2 U}{\partial x_A \partial x_B}\,\delta x_A \delta x_B > 0. \tag{63.7}$$

Strictly speaking, for satisfying condition (63.6) it would suffice for the quadratic form $\frac{\partial^2 U}{\partial x_A \partial x_B}\,\delta x_A \delta x_B$ to be non-negative, and for values x_A at which it vanishes the third-order form from the development of $(\delta\Phi)_X$ would be zero, while the fourth order form would be positive. The quadratic form becomes zero at a critical point. We eliminate this case from our consideration, so that all the subsequent conclusions are valid on the assumption of a non-critical state of the crystal.

If partial derivatives $\partial^2 U/\partial X_A \partial x_B$ are calculated with $y_A = 0$ ($A = 0, \ldots, 9$), they become the elements of thermodynamic matrix N. Therefore the following inequality should hold as a particular case of inequality (63.7)

$$N_{AB}\,\delta x_A \delta x_B > 0. \tag{63.8}$$

Since increments δx_A are arbitrary, it is necessary for the fulfilment of inequality (63.8) that matrix N should be positively definite.

It is known that a positively definite matrix always has its reciprocal, the latter also being positively definite. Thus the matrix M is positively definite too.

According to Sylvester's theorem, all the principal minors of positively definite matrices are positive. The *principal minors* of a matrix are the determinant of the matrix itself and all determinants obtained from the first one by crossing out rows and columns of the same number (e.g. the first row and the first column or the last three rows and the last three columns, etc.). In particular, any element on the principal diagonal of the matrix is a principal minor. Therefore in thermodynamic matrices M and N all the coefficients

located on the principal diagonal are essentially positive*.

$$C_p > 0, \quad C_v > 0,$$

$$\begin{array}{llllll} \varkappa_{11} > 0, & \varkappa_{22} > 0, & \varkappa_{33} > 0, & \eta_{11} > 0, & \eta_{22} > 0, & \eta_{33} > 0, \\ s_{11} > 0, & s_{22} > 0, & s_{33} > 0, & c_{11} > 0, & c_{22} > 0, & c_{33} > 0, \\ s_{44} > 0, & s_{55} > 0, & s_{66} > 0, & c_{44} > 0, & c_{55} > 0, & c_{66} > 0. \end{array} \tag{63.9}$$

The values of the components of tensors change under transition from one reference frame to another. Since the coordinate system was in no way fixed in the derivation, these inequalities are valid in any one of them.

It follows, in particular, that the normal components $\boldsymbol{q}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{q}$, and $\boldsymbol{q}\cdot\boldsymbol{\eta}\cdot\boldsymbol{q}$ are positive at any $\boldsymbol{q}$. Indeed, accepting the unit vector $\boldsymbol{q}$ to be directed along axis $\boldsymbol{e}_1$ of some coordinate system, we obtain in this system $\boldsymbol{q}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{q} = \varkappa_{11}$ and $\boldsymbol{q}\cdot\boldsymbol{\eta}\cdot\boldsymbol{q} = \eta_{11}$.

The positiveness of Young's modulus $E(\boldsymbol{q})$ and of shear modulus in twisting $G(\boldsymbol{q})$ at any unit vector $\boldsymbol{q}$ is proved similarly.

Let us now consider the principal minors of the second order. Their positiveness means that the non-diagonal elements of the matrices M and N must be bounded in their absolute value. For example, from

$$\begin{vmatrix} s_{11} & s_{12} \\ s_{12} & s_{22} \end{vmatrix} > 0$$

it follows that

$$s_{12}^2 < s_{11}s_{22}. \tag{63.10}$$

Similarly we obtain

$$\varkappa_{12}^2 < \varkappa_{11}\varkappa_{22}. \tag{63.11}$$

This condition also bounds the absolute value of the coefficients of thermal expansion, and of pyroelectric and piezoelectric coefficients. Thus from

$$\begin{vmatrix} C_p/T_0 & \alpha_1 \\ \alpha_1 & s_{11} \end{vmatrix} > 0$$

there follows an inequality for the thermal expansion coefficient

$$\alpha_1^2 < \frac{C_p s_{11}}{T_0}. \tag{63.12}$$

* In the first two inequalities we used the positiveness of the absolute temperature.

Inequalities for pyroelectric and piezoelectric coefficients are derived similarly, for instance

$$p_1^2 < \frac{C_p \varkappa_{11}}{4\pi T_0}, \tag{63.13}$$

$$d_{14}^2 < \frac{\varkappa_{11} s_{44}}{4\pi}. \tag{63.14}$$

In the same way there are obtained the inequalities for adiabatic coefficients—the elements of matrix N, for example

$$c_{12}^2 < c_{11} c_{22}, \tag{63.15}$$

$$\eta_{12}^2 < \eta_{11} \eta_{22}, \tag{63.16}$$

$$\beta_1^2 < \frac{T c_{11}}{C_v}, \tag{63.17}$$

$$q_1^2 < \frac{4\pi T \eta_{11}}{C_v}, \tag{63.18}$$

$$h_{12}^2 < 4\pi \eta_{11} c_{22}. \tag{63.19}$$

The physical meaning of these coefficients is clear from formulas (60.12); their names are given there (in Sec. 60) too.

We shall consider the use of the principal minors of the third order in the derivation of thermodynamic inequalities in the instance of the elastic properties of cubic crystals and isotropic bodies.

The positiveness of the principal minors of the first order gives an already known result

$$s_{11} > 0, \tag{63.20}$$

The positiveness of the second-order principal minors which for the cubic crystals have the form

$$\begin{vmatrix} s_{11} & s_{12} \\ s_{12} & s_{11} \end{vmatrix} > 0,$$

results in inequality $s_{11}^2 > s_{12}^2$; taking account of (63.20) we can write it down in the form

$$-s_{11} < s_{12} < s_{11}. \tag{63.21}$$

The condition for the positiveness of the third-order principal minor for cubic crystals is

$$\begin{vmatrix} s_{11} & s_{12} & s_{12} \\ s_{12} & s_{11} & s_{12} \\ s_{12} & s_{12} & s_{11} \end{vmatrix} > 0,$$

or, which is just the same,

$$s_{11}^3 + 2s_{12}^3 - 3s_{11}s_{12}^2 > 0,$$

which upon factorization of the polynomial in the left-hand side appears as

$$(s_{11}-s_{12})^2(s_{11}+2s_{12})>0.$$

Hence it follows that $s_{11}+2s_{12}>0$ or $s_{12}>-s_{11}/2$, this allowing an essential refinement of inequality (63.21) for the cubic crystals:

$$-\frac{1}{2}s_{11}<s_{12}<s_{11}. \tag{63.22}$$

For the description of elastic properties of isotropic bodies there are commonly used Young's modulus $E=1/s_{11}$ and Poisson's ratio $\nu=-s_{12}/s_{11}$. The well-known inequality for Poisson's ratio for isotropic bodies follows from (63.22):

$$-1<\nu<\frac{1}{2}. \tag{63.23}$$

Inequalities following from the positiveness of the second- and higher-order minors can also be expressed in an invariant form. For instance, it follows from the inequality $4\pi d_{11}^2<\varkappa_{11}s_{11}$ that with an arbitrary unit vector $\boldsymbol{q}$

$$4\pi\,(\boldsymbol{q}\cdot\mathbf{d}:\boldsymbol{qq})^2<(\boldsymbol{q}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{q})\;(\boldsymbol{qq}:\mathbf{s}:\boldsymbol{qq}); \tag{63.24}$$

this inequality shows that the electromechanical coupling coefficient for the longitudinal piezoelectric effect in an arbitrary direction is less than unity. It can be easily proved that all possible electromechanical coupling coefficients at arbitrary orientations of the electric field and mechanical stresses are also less than unity.

Sec. 64. Alteration of Crystal Symmetry in Phase Transitions of the Second Kind

There are known fairly many chemical substances which can exist in several crystal modifications; each modification is stable within a definite temperature range*. Under temperature variations such substances experience phase transitions. In the majority of cases these are the *transitions of the first kind*, in which crystal structure changes jumpwise with corresponding abrupt changes of the state of the substance.

However, phase transitions between two different (i.e. possessing different symmetries) crystal modifications of one and the same substance can occur in another way. The point is that for one case of the alteration of symmetry, i.e. for its reduction, there would suffice any arbitrarily small displacements of particles from the points of their original special position.

* Strictly speaking, in a definite region on a plane with temperature and pressure as coordinates.

Thus, any arbitrarily small displacement of particles located in the centres of symmetry of a crystal structure results in the latter losing its centres of symmetry. If particles located on the axes or symmetry planes are displaced from these axes or planes, the structure loses these symmetry elements; it retains them only when the displacements of particles occur within a symmetry plane or along a symmetry axis.

When crystal symmetry alters as a result of an infinitesimal alteration of crystal structure, and therefore the state of a body alters continuously and not jumpwise, the phase transition is called the *phase transition of the second kind.*

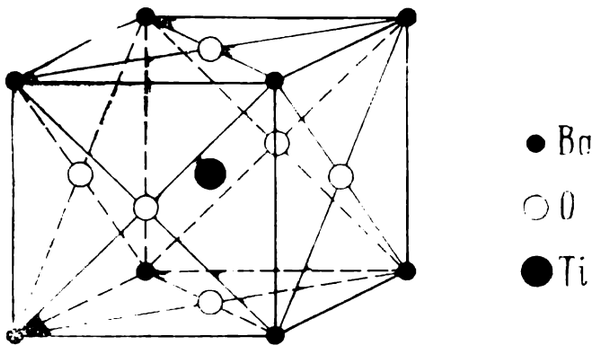


Fig. 64.1. Structure of the cubic modification of barium titanate

Actually, we can never be sure that the displacement of atoms causing the reduction of symmetry is truly infinitesimal; we can only say that it is so small that the accuracy of our instruments is not sufficient to detect a jump. Sometimes we are even able to detect a jump though it is small; in these cases it is said that the phase transition, even though being of the first kind, is close to that of the second kind. Exactly such, in particular, is the phase transition occurring in barium titanate. Let us consider it in more detail.

Fig. 64.1 shows the structure of the cubic modification of barium titanate, $BaTiO_3$. Its space group is $Pm3m$, its point group is $m3m$. This modification exists at a temperatures exceeding 120°C. When the temperature drops below 120°C, the atoms of titanium and oxygen begin shifting with respect to atoms of barium in the direction of one of the cube edges.

It is quite evident that as soon as this small shifting begins, the crystal symmetry instantly reduces: the space group decreases to $P4mm$, the point group to $4mm$. Thus at the given temperature barium titanate transforms into a tetragonal modification. At temperatures close to that of the phase transition there is but little deviation from the cubic structure. As temperature drops still lower, the alteration of structure gradually increases, but even at room temperature, i.e. about 100°C below the transition point, the maximum shifts of atoms from their "cubic" positions do not increase to more than 0.03 of the cell parameter, while the axial ratio c/a differs from unity still less.

The reduction of symmetry in barium titanate is caused by the shifting of atoms, therefore such transitions are called the *transitions of the displacement type.* Quite another mechanism of the reduction

of symmetry is active in phase transitions of the second type—of the "order-disorder" type. Let us acquaint ourselves with them in the example of the transition of the second kind in CuZn alloy.

At sufficiently high temperatures this alloy forms a body-centred cubic structure (structural type α-Fe): the atoms of copper and zinc occupy, with perfectly equal probabilities, the points of a body-centred Bravais cubic lattice; the space group of this structure is $Im3m$. However, at a certain temperature drop such an array of atoms is more stable thermodynamically when in the first coordination sphere of a given atom the occurrence of an opposite atom is more probable than that of the same one. It is just at this moment that the crystal symmetry alters, even though the change in the array of atoms is extremely small. The tendency of each atom to have predominantly opposite atoms for its closest neighbours produces the following results: if we mentally divide a not too large (but still macroscopic) part of the crystal structure into two simple cubic lattices, inserted one into the other, we shall find atoms of prevalently one kind at the points of one sublattice, and atoms of another kind at the points of the other, this meaning that the sublattices are not symmetrically equivalent to each other: the structure has lost translations which connected the cube vertices with the centres. Thus, an infinitesimal change in the array of atoms reduced the translation symmetry by 50 per cent; the Bravais lattice of the new, partially ordered lattice is a primitive cubic one, the space group is $Pm3m$.

We want to emphasize that even an infinitesimal difference between the probabilities for different kinds of atoms to be at the points of a given sublattice is sufficient for the described reduction of symmetry. As the temperature drops further, the probabilities differ still more, the ordering of the crystal increases, approaching a complete ordering when one sublattice contains atoms of one kind exclusively and the other sublattice has atoms of only another kind. But the crystal symmetry does not alter any more: a fully ordered and a slightly ordered crystal have the same space group $Pm3m$, and only a totally disordered crystal has a higher space group, namely $Im3m$.

The reviewed examples show how with any arbitrarily small alteration of the structure the symmetry transforms jumpwise. Besides, these examples help to understand that the modifications connected by a phase transition of the second kind are not equivalent to each other: one of them is more symmetric than the other. Let us agree to call the first modification *symmetric*, and the second one *dissymmetric*.

Thus a space group of the dissymmetric modification is a subgroup of a space group of the symmetric modification. Moreover, the space groups of crystal modifications should satisfy a few more requirements (see Sec. 66) besides the above ones.

Table 64.1

Some Phase Transitions of the Second Kind and Those Close to Them

Substance		Transition temperature, °C	Symmetric modification		Dissymmetric modification		Reduction of symmetry			Character of transition
name	synonym and formula		space group	class	space group	class	rotation	translation	total	
Barium titanate	$BaTiO_3$	120	$Pm3m$	$m3m$	$P4mm$	$4mm$	6	1	6	disp, fe, Ik
Rochelle salt	$NaKC_4H_4O_6 \cdot 4H_2O$	24-18	$P2_12_12$	222	$P2_1$	2	2	1	2	ord+disp, fe
Triglycinsulphate	$(CH_2NH_2COOH)_3 \cdot H_2SO_4$	49	$P2_1/m$	$2/m$	$P2_1$	2	2	1	2	ord+disp, fe
Potassium dihydrophosphate (KDP)	KH_2PO_4	151	$I\bar{4}2d$	$\bar{4}2m$	$Fdd2$	$mm2$	2	1	2	ord+disp, fe
Potassium hexaferrocyanide, trihydrate	$K_4Fe(CN)_6 \cdot 3H_2O$	−25	$C2/c$	$2/m$	Cc	m	2	1	2	ord+disp, fe
Ammonium sulphate	$(NH_4)_2SO_4$	−49	$Pnam$	mmm	$Pna2_1$	$mm2$	2	1	2	fe, Ik
Dicalcium strontium propionate	$Ca_2Sr(CH_3CH_2COO)_6$	8.5	$P4_32_12$ / $P4_12_12$	422	$P4_3$ / $P4_1$	4	2	1	2	fe
Ammonium dihydrophosphate (ADP)	$NH_4H_2PO_4$	−125	$I\bar{4}2d$	$\bar{4}2m$	$P2_12_12_1$	222	2	2	4	ord+disp
Tungsten trioxide	WO_3	900	$Pm3m$	$m3m$	$P4/nmm$	$4/mmm$	3	2	6	disp
Quartz	SiO_2	573	$P6_222$ / $P6_422$	622	$P3_121$ / $P3_221$	32	2	1	2	disp
Potassium nitrate	$NaNO_3$	275.5	$R\bar{3}m$	$\bar{3}m$	$R\bar{3}c$	$\bar{3}m$	1	2	2	ord
Brass	CuZn	450	$Im3m$	$m3m$	$Pm3m$	$m3m$	1	2	2	ord
Heyssler alloy	Cu_2MnAl		$Im3m$	$m3m$	$Fm3m$	$m3m$	1	4	4	ord

Abbreviations: disp–transition accompanied by displacement of atoms; ord–transition connected with ordering; fe–ferroelectric transition. Ik–transition of the first kind.

The disparity between the symmetric and dissymmetric modifications is manifested especially obviously in the approach of the structure of the dissymmetric modification to that of the symmetric one as the temperature reaches the phase transition point T_c, while as the temperature recedes from T_c, the dissymmetric modification diverges more and more from the symmetric one; on the contrary, up to the very transition point there occur no alterations in the structure of the symmetric modification which would bring it nearer to the structure of the dissymmetric one*. Figuratively speaking, the symmetric modification is "ashamed" of its kinship with the dissymmetric one, while the latter is not at all "ashamed" of the kinship.

Table 64.1 gives several examples of phase transitions of the second kind or those close to them. In the simple cases considered above the reduction of symmetry was caused only by the shifting of atoms or only by their ordering; in some transitions, as can be seen from the Table, both mechanisms operate simultaneously**.

Numbers in the column giving the reduction of the rotation symmetry show how many times the symmetry was reduced under transition or, to be more precise, the subgroup of each index is the point group of the less symmetric phase with respect to the point group of the more symmetric phase. In the next column it is shown how many times the translation symmetry is reduced under transition, i.e. how many times the volume of an elementary cell (or, to be more accurate, the number of atoms in it) is increased. Finally, a number in the third column, equal to the product of the numbers in the first and second columns, shows whose subgroup index is the space group of the dissymmetric modification with respect to the space group of the symmetric modification. Table 64.1 shows examples of transitions under which rotation symmetry alone is altered (quartz, barium titanate, Rochelle salt, triglycinesulphate, potassium dihydrophosphate), translation symmetry alone (self-ordering alloys, sodium nitrate) and, finally the two symmetries together (ammonium dihydrophosphate, tungsten trioxide).

Transitions occurring without the alteration of the translation symmetry (Indenbohm, 1960) are the phase transitions of the second kind which are very widespread and important for practical use. Fig. 64.2 shows all the possible alterations of symmetry occurring under transitions of this type. There are all in all 90 versions of such alterations; 58 of them are characterized by the reduction of the point group order by 50 per cent, 9—by reduction of it by 75 per

---

* We want to emphasize that only structure is meant here: as the Curie point is approached, there appear indications of this in the symmetric phase (see Barfoot, 1967), but this is not a transformation of structure.

** It is believed that the initiating factor in such transitions is the ordering, while the shifting of atoms is merely its consequence.

cent, 19—to one sixth, and 4 versions, to one eighth of the original value.

Less symmetric ordered modifications correspond in the majority of cases to low temperatures, more symmetric disordered modifications correspond to high temperatures, but this empirical rule is not always fulfilled. For instance, the dissymmetric modification of Rochelle salt transforms to the symmetric one not only when temperature rises to +24°C, but also when it drops to —18°C.

If a space group of the dissymmetric modification is a subgroup of index n with respect to a group of the symmetric modification, then

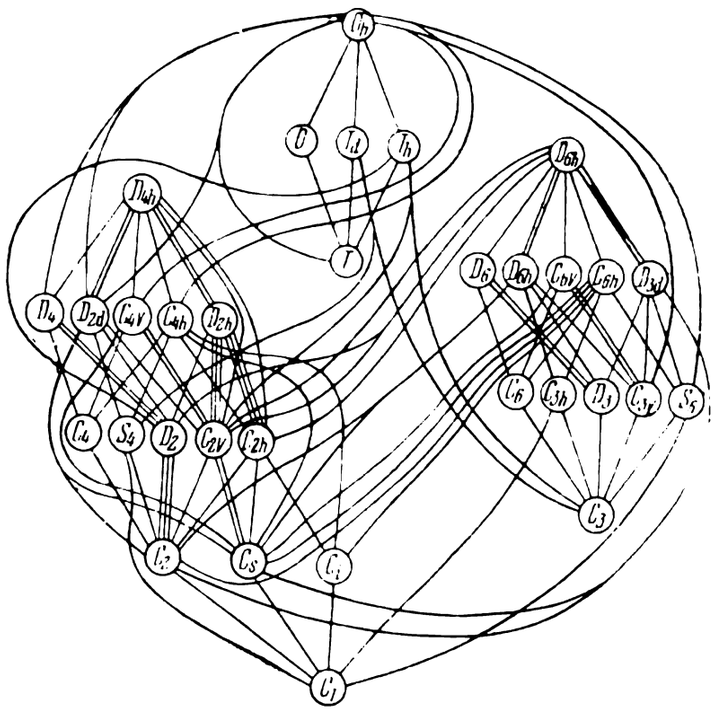


Fig. 64.2. Changes of crystal symmetry in phase transitions of the second kind, occurring without changing the number of atoms in an elementary cell. The lines connect crystallographic classes between which transitions are possible. Straight lines are for a two-fold alteration of symmetry in a transition, curves are for greater than two-fold alterations of symmetry, double and triple lines mean that the transition can occur in two or three ways (Indenbohm, 1960

the more symmetric modification changes to the less symmetric one by n ways. In such a transition the crystal is usually divided into parts which are called *domains*, in each of which the transition is realized by one of the n ways; altogether n types of domains are formed. Symmetry operations contained in the space group of the dissymmetric modification transform each domain into itself. The symmetry operations contained in the space group of the symmetric modification, but not contained in the space group of the dissymmetric modification, in other words, those symmetry operations which

the crystal loses as a result of the transition, transform a domain of one type into a domain of another type.

If the translation symmetry of the crystal does not vanish upon transition, the domains of one type transform into those of another type under some simple or inversion rotations, namely under those

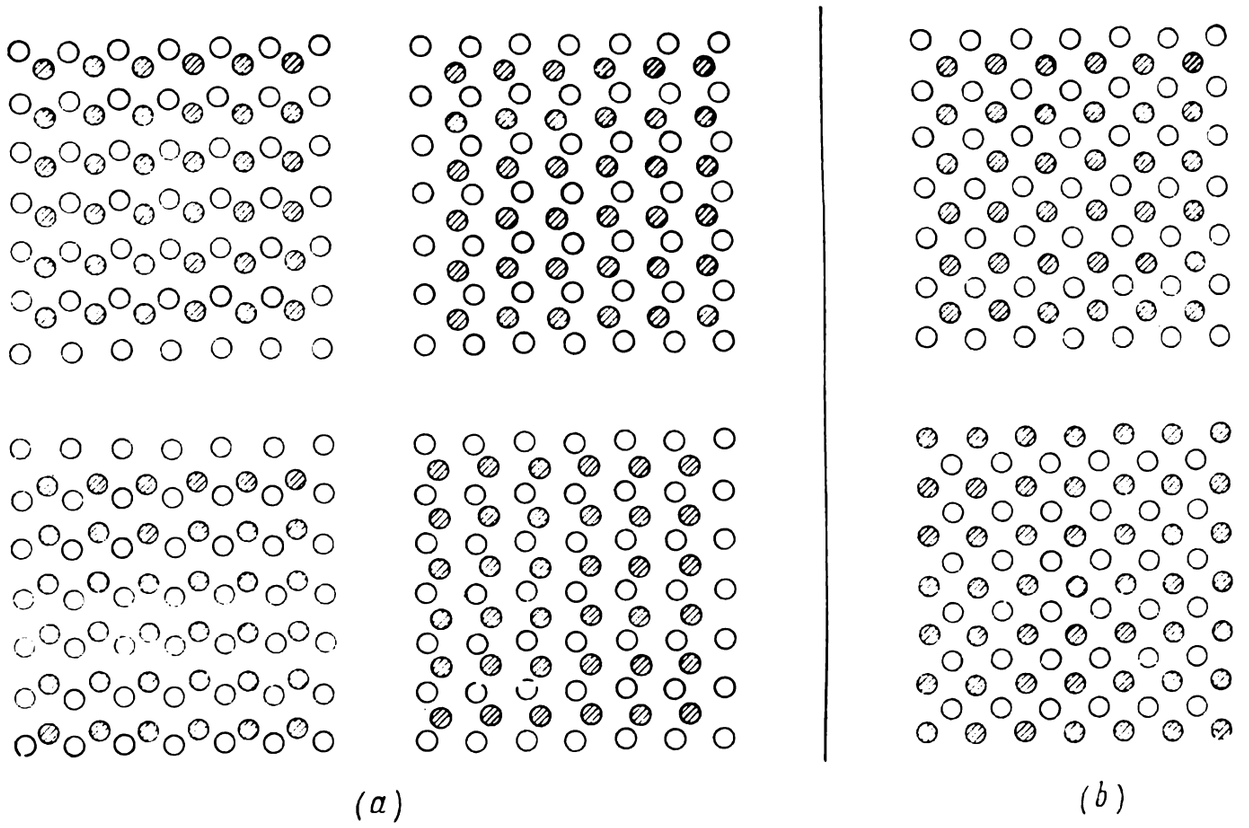


Fig. 64.3. Schematic diagram of the division of a crystal into domains in phase transitions of the second kind: (a) two-dimensional analogue of the transition in barium titanate—four types of domains transforming one into another at a 90° rotation (actually six types of domains are formed in this case); (b) two-dimensional analogue of the transition in a CuZn alloy—two types of domains transforming one into another under translations which are lost in transitions (in an actual transition two types of domains are formed)

which were lost in the transition. But if only the translation symmetry, and not the rotation one, alters in transition, then the domains of different types transform one into another not under rotations, but under translations, again under those which were lost in the transition. It can be said that in the first case the domains of one type are turned about with respect to those of another type, and in the second case they are shifted with respect to them. The cases are shown in Fig. 64.3.

At first sight the phase transitions of the second kind, in which crystal symmetry is reduced, contradict the Curie principle: "When definite dissymmetry is found in some phenomena, the same dissymmetry should be found in the causes

that produced them"*, but in the present case the reduction of crystal symmetry occurs as a result of temperature variations—a cause obviously lacking the required dissymmetry. This paradox is explained by the fact that on the average the crystal symmetry is not reduced in such transitions at all. In a volume containing sufficiently many domains there are represented, in approximately equal shares, all possible ways of transitions, i.e. all possible types of domains; therefore the symmetry of a volume upon transition is the same as prior to it**. True enough, it happens sometimes that as a result of transitions crystals become monodomainial. Upon the examination of a sufficiently large number of crystals which experience transition, we shall see that the symmetry of all their multitude on the whole was not reduced due to temperature variations; this was to be expected.

The case of phase transitions of more symmetric crystal modifications into less symmetric ones shows that sometimes the Curie principle is not directly applicable to a single object, but then this object can be regarded as an element of a certain statistical group for which the Curie principle is perfectly valid.

The Curie principle forbids some phenomena, but by no means demands actual occurrence of the phenomena it permits; thus, it forbids the centrosymmetric crystals to display piezoelectrical properties, but therefrom by no means follows that non-centrosymmetric crystals must display such properties. The analogy is readily seen here with the principles of thermodynamics which also forbid some phenomena and also do not demand the actual occurrence of the permitted ones. The similarity of the Curie principle to the principles of thermodynamics does not end here; in the example of phase transitions of the second kind we see that the Curie principle as well as the second principle of thermodynamics, has a statistical character. However, the main feature uniting the Curie principle with the principles of thermodynamics is their extensive generality; as well as the principles of thermodynamics the Curie principle represents not even a physical law, but one of the most general laws of natural science. It is just for this reason that Marie Curie, in conclusion of her review of the works of Pierre Curie on the theory of symmetry and the physics of crystals, speaks of "the great philosophic meaning of the concepts of symmetry that penetrate into the very essence of all the phenomena of nature..." (M. Curie, 1955, p. 25).

Sec. 65. Changes of the Physical Properties of Crystals Under Phase Transitions of the Second Kind

To describe a crystal experiencing a phase transition of the second kind L. D. Landau (1937)*** introduced a quantity η which determines the degree of the divergence of the array of atoms in the dissymmetric phase from their array in the symmetric phase; $\eta = 0$ corresponds to the symmetric phase, while in the dissymmetric phase η assumes non-zero positive or negative values. We shall call this quantity a *parameter of dissymmetry*. Since crystal structure alters continuously under the transition of the second kind, the dissymmetry parameter can have any arbitrarily small values.

* P. Curie (1909, p. 102)

** Therefore there is always meant under the symmetry of a dissymmetric modification not the symmetry of a polydomainial crystal, but the symmetry of a domain.

*** See also Landau and Lifshits (1976).

In transitions connected with the shift of atoms η can be understood as the magnitude of the shift. Thus, under the transition in barium titanate it is natural to believe the parameter of dissymmetry to be equal to the ratio between the shift of a titanium atom u_{Ti} from the centre of a regular tetragonal prism, formed by the barium atoms nearest to it, and the edge a of the elementary cell of the cubic modification: $\eta = u_{Ti}/a$.

In the transitions connected with ordering the parameter of dissymmetry can be assumed equal to the degree of ordering, i.e. to the quantity which shows to what extent is probable the location in a given sublattice of an atom of one kind than of the other. If, for instance, in the above discussed transition of the second kind in brass the corresponding probabilities are denoted by w_{Cu} and w_{Zn}, then $\eta = (w_{Cu} - w_{Zn})/(w_{Cu} + w_{Zn})$.

In this Section we confine ourselves to the discussion of the phase transition of the second kind occurring with the reduction of symmetry by 50 per cent. In this case only two types of domains are formed: to one type there correspond positive values of the dissymmetry parameter, to the other type—negative values of the parameter. Evidently, the dissymmetry parameter is invariant with respect to all symmetry operations which transform each type of domain into itself, i.e. with respect to the space group of the dissymmetric phase. The symmetry operations of the space group of the symmetric phase which are not included into the space group of the dissymmetric phase, as was already noted, transform the domains of one type into those of the other; since the dissymmetry parameter has opposite signs in the domains of different types, it is multiplied by —1 as a result of such operations.

Apparently, all possible even functions of the parameter dissymmetry, in particular its even powers, are the invariants of the space group of the symmetric phase. Also invariant with respect to this group are the products of the even functions of the parameter of dissymmetry multiplied by the expressions, composed of the components of thermodynamic forces invariant with respect to the space group of the symmetric phase. It should be remembered that due to the invariance of thermodynamic forces and coordinates with respect to translations, the expressions composed of their components are invariant with respect to the space group of the crystal if and only if they are invariant with respect to its point group (Secs. 25 and 44).

There is, however, another type of invariants: the products of the parameter of dissymmetry (or its odd functions, in particular, odd powers) by such expressions, composed of the components of thermodynamic forces or coordinates, which transform in the same way as the parameter of dissymmetry. Let $K_a X_a$ and $L_{ab} X_a X_b$ be just

such functions of the generalized forces*: they are invariant with respect to the operations which are retained in the transition to the dissymmetric phase and multiplied by —1 in case of operations which are lost in the transition. The coefficients K_a and L_{ab} can be naturally compared with the elements of the thermodynamic potential matrix M (see Secs. 57, 58, 60): the coefficients L_{ab} correspond to elements M_{ab} with the same indices, while K_a, to elements M_{0a} and M_{a0}. Let us consider that not the thermodynamic forces X_a but the coefficients K_a and L_{ab} are transformed; then the problem will consist in finding such elements of the matrix M which are invariant with respect to the point group of the dissymmetric phase G_D and reverse their sign under the action of all other operations of the point group of the symmetric phase G. Because of the twofold alteration of symmetry in this case it can be easily shown that from components of the tensors invariant with respect to the group G_D (in particular, from coefficients K_a and L_{ab}) it is possible to compose such linear combinations which are either invariant with respect to all the operations of the group G or are invariant only with respect to G_D and reverse their sign** under the operations from $G - G_D$. The total number of independent linear combinations of both types is equal to the number of the independent components of a corresponding tensor which is invariant with respect to the group G_D. Thus, if we compare the general forms of tensors invariant with respect to the group G_D and its subgroup G_D, we see that those components (or their linear combinations) which are invariant with respect to G_D and are multiplied by —1 as a result of the operations from $G - G_D$ complement the general form of the tensor invariant with respect to G_D up to the general form of the tensor invariant with respect to G_D. Apparently, coefficients K_a and L_{ab} also complement the general form of matrix M which is invariant with respect to G up to the general form of the matrix invariant with respect to G_D (see Table 58.5). Symbolic equalities

$$K_a(G/G_D) = M_{0a}(G_D) - M_{0a}(G),$$
$$L_{ab}(G_0/G_D) = L_{ab}(G_D) - L_{ab}(G)$$

describe a graphic method, based on the above, for the determination of the coefficients K_a and L_{ab} for the phase transition of the second kind between groups G and G_D; the scheme of the symmetric phase matrix is "subtracted" from the scheme of the dissymmetric phase

* Here, as in the preceding Sections, X are the generalized thermodynamic forces, but in distinction from indices A, B, C, D which can have ten values: $A, B, C, D = 0, 1, \ldots, 9$, we introduce indices a, b, c, d which can have only nine values: $a, b, c, d = 1, \ldots, 9$.

** The symbol $G - G_D$ denotes the totality of the elements of the group G which are not contained in its subgroup G_D. Let it be emphasized that $G - G_D$ is not a group.

matrix M: the "difference" is the scheme of coefficients K and L (Fig. 65.1).

It must only be borne in mind that the scheme of the dissymmetric phase matrix can differ from the standard one. The point is that the coordinate system in which the dissymmetric phase is specified is predetermined by the choice of the coordinate system for the symmetric phase. If the symmetric phase is specified in the crystal-physical system of coordinates, as it is usually done, the coordinate system for the dissymmetric phase may occur to be not crystal-physical.

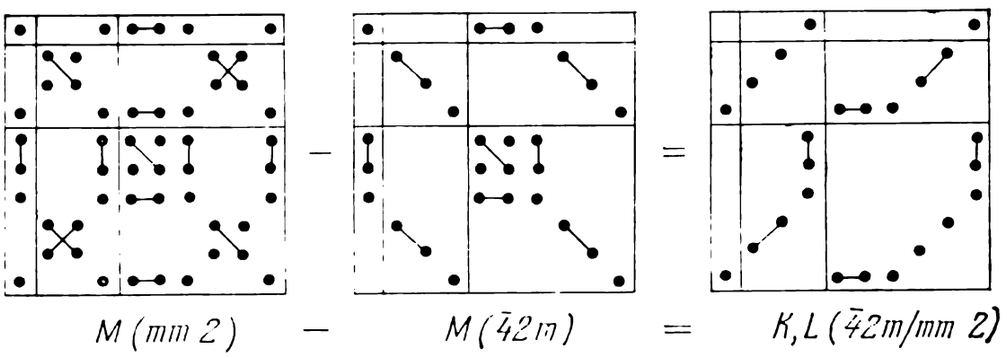


Fig. 65.1. Graphic determination of coefficients K_a and L_{ab} for a phase transition of the second kind in a crystal of potassium dihydrophosphate, $G = \bar{4}2m$, $G_D = mm2$

This is just what happens in the transitions in Rochelle salt and potassium dihydrophosphate. In the former case the departure from the crystal-physical coordinate system consists in the renaming of the axes ($G_D = 2 \parallel X_1$) and, correspondingly, in the rearray of some rows and columns in matrix M (G_D); when this is borne in mind, the matrix can be easily obtained from the standard one. In the latter case the coordinate system is rotated by 45° with respect to the crystal-physical one ($G_D = mm2$, $2 \parallel X_3$, $m \perp (e_1 \pm e_2)/\sqrt{2}$), as a result of which the scheme of matrix M (G_D) essentially differs from the standard one; it is shown in Fig. 65.1, while relations connecting it with the standard matrix (Table 58.5) are given in Sec. 85.

We shall regard the thermodynamic potential of a crystal, for a definite parameter of dissymetry η as a function of thermodynamic forces $\theta = T - T_c$, E_i, σ_λ and this parameter: $\Phi = \Phi(\Theta, \boldsymbol{E}, \boldsymbol{\sigma}; \eta)$. However, the number of independent variables here is not 11 but only 10: for the specified thermodynamic forces the corresponding parameter of dissymmetry is defined from the condition of thermodynamic equilibrium i.e. from the minimal value of the thermodynamic potential.

It may seem that the thermodynamic potential at $\eta = 0$ is invariant with respect to the point group of the symmetric modification, while at $\eta \neq 0$ it is invariant with respect to the point group of the dissymmetric modification. This is not so. Actually the thermodyna-

mic potential must remain invariant with respect to a higher point group at $\eta \neq 0$, since it describes not merely a single method of the reduction of symmetry, but all such methods and correspondingly all types of domains.

In the particular case of a two-fold reduction of symmetry, which is the only case we discuss here, there are formed two types of domains. Positive values of η correspond to one of them, and negative values to the other, and both of them must be equally specified by the thermodynamic potential. It is clear therefore that in the absence of an electric field and mechanical stresses the expansion of the thermodynamic potential with respect to the powers of the dissymmetry parameter, if at all permissible, contains only even powers of this parameter:

$$\Phi = \Phi_0 + A\eta^2 + B\eta^4 + \ldots; \tag{65.1}$$

the coefficients of this expansion Φ_0, A and B are functions of temperature*.

The point of transition of the second kind is probably a singular point of the thermodynamic potential; therefore the permissibility of expansion (65.1) has not been proved. In a number of cases, however, inferences from this expansion well agree with experimental data.

Equilibrium conditions call for a minimal value of thermodynamic potential:

$$\frac{\partial \Phi}{\partial \eta} = 2A\eta + 4B\eta^3 = 0, \tag{65.2}$$

$$\frac{\partial^2 \Phi}{\partial \eta^2} = 2A + 12B\eta^2 > 0. \tag{65.3}$$

Condition (65.2) is satisfied by three values of the dissymmetry parameter:

$$\eta = 0, \quad \eta = \pm \sqrt{-A/(2B)}. \tag{65.4}$$

The solution $\eta = 0$ corresponds to the symmetric modification. It follows from condition (65.3) that in this modification $A > 0$.

Solution (65.4) on the contrary, corresponds to the dissymmetric modification, to both types of its domains. It can be seen from the form of the solution that in this modification coefficients A and B have opposite signs, while it follows from condition (65.3) that in this modification $A < 0$; consequently $B > 0$.

Thus at the transition point coefficient A reverses its sign. As a first approximation

$$A = a\,(T - T_c), \tag{65.5}$$

* This argument is applicable only in this particular case. For the general case see Landau and Lifshits (1976).

where T_c is the temperature of the phase transition of the second kind also called the Curie temperature or the *Curie point*. If the symmetric modification corresponds to a higher temperature, the coefficient a is positive, in the opposite case it is negative.

At the Curie point $\partial^2\Phi/\partial\eta^2 = 0$. For the thermodynamic potential to be at its minimum at this point, conditions $\partial^3\Phi/\partial\eta^3 = 0$, $\partial^4\Phi/\partial\eta^4 = 0$ must be fulfilled. Hence it follows that at the Curie point $B > 0$ too. Because of its continuity this coefficient is positive within a certain range of temperatures near the transition point also in the symmetric modification. As a first approximation we shall simply consider it as a positive constant.

Thus in the dissymmetric modification

$$\eta = \pm \sqrt{\frac{a(T_c - T)}{2B}}, \tag{65.6}$$

where a and B as a first approximation do not depend on temperature. This formula defines the dependence of the dissymmetry parameter on temperature characteristic of the transitions of the second kind: $\eta \sim |T - T_c|^{1/2}$.

So now expansion (65.1) has the form

$$\Phi = \Phi_0(T) + a\Theta\eta^2 + B\eta^4 + \ldots, \tag{65.7}$$

where $\Theta = T - T_c$. If a crystal is placed in an electric field or experiences mechanical stresses, this expansion must be supplemented with terms that depend on the components of the electric field vector $E_i = X_i$ and the stress tensor $\sigma_\lambda = X_{3+\lambda}$ and are invariant with respect to the point group of the symmetric modification. Such terms can be divided into three types.

1. Invariants composed of the components Θ and X_b of the generalized thermodynamic forces*. All together they constitute sums of the form $R_b^{(0)}\,\Theta\,X_b$ and $M_{bd}^0 X_b X_d$. Here $R_b^{(0)}$ and $M_{bd}^{(0)}$ have the same form and satisfy the same relations as the elements of the thermodynamic matrix M_{BD} (B, $D = 0, 1, \ldots, 9$) of the given crystallographic class (see Table 58.5), $R_b^{(0)}$ corresponding here to the elements M_{0b} and M_{b0}, and $M_{bd}^{(0)}$ to the elements M_{bd}.

2. Products of the invariants of the generalized thermodynamic forces multiplied by the invariants of the dissymmetry parameter. We shall be concerned only with those of them which are contained in the sum $Q_b X_b \eta^2$. Obviously, coefficients Q_b have the same form and satisfy the same relations as $R_b^{(0)}$.

3. Invariants composed of the products of the dissymmetry parameter by the generalized thermodynamic forces and their quadratic combinations. All together they constitute sums of the form $K_b X_b \eta$ and $L_{bd} X_b X_d \eta$, discussed in detail above. Sums of the form $H_b \Theta X_b \eta$

* Here indices a, b, c, d assume values 1, ..., 9 as in the preceding Section.

belong to the same type of invariants, but we shall not consider them, since at temperatures close to the Curie point they are but minor additions to the sums $K_b X_b \eta$.

Thus we arrive at the following expansion of the thermodynamic potential of a stressed crystal placed in an electric field in the vicinity of the Curie point:

$$\Phi = \Phi_0(T) - R_b^{(0)}\Theta X_b - \frac{1}{2} M_{bd}^{(0)} X_b X_d + a\Theta\eta^2 + \\ + B\eta^4 - K_b X_b \eta - \frac{1}{2} L_{bd} X_b X_d \eta - Q_b X_b \eta^2. \qquad (65.8)$$

The parameter of dissymmetry η is determined from the condition of thermodynamic equilibrium

$$\frac{\partial\Phi}{\partial\eta} = 2a\Theta\eta + 4B\eta^3 - K_b X_b - \frac{1}{2} L_{bd} X_b X_d - 2Q_b X_b \eta = 0. \qquad (65.9)$$

The value of this parameter in the absence of electric field and mechanical stresses

$$\eta_0 = \begin{cases} 0 & \text{in the symmetric phase,} \\ \pm\sqrt{-\dfrac{a\Theta}{2B}} & \text{in the dissymmetric phase.} \end{cases} \qquad (65.10)$$

Having differentiated equality (65.9) with respect to T and to X_b, we obtain

$$\frac{\partial\eta}{\partial T} = -\frac{2a\eta}{2a\Theta + 12B\eta^2 - 2Q_b X_b}, \\ \frac{\partial\eta}{\partial X_b} = \frac{K_b + L_{bd} X_d + 2Q_b\eta}{2a\Theta + 12B\eta^2 - 2Q_b X_b}. \qquad (65.11)$$

Substituting $\eta = \eta_0$ in these formulas and assuming $X_b = 0$ we find the values of the corresponding derivatives for very weak electric fields and mechanical stresses:

$$\left(\frac{\partial\eta}{\partial T}\right)_0 = \begin{cases} 0 & \text{in the symmetric phase,} \\ \dfrac{\eta_0}{2\Theta} & \text{in the dissymmetric phase;} \end{cases} \\ \left(\frac{\partial\eta}{\partial X_b}\right)_0 = \begin{cases} \dfrac{K_b}{2a\Theta} & \text{in the symmetric phase,} \\ -\dfrac{K_b + 2Q_b\eta_0}{4\Theta a} & \text{in the dissymmetric phase.} \end{cases} \qquad (65.12)$$

Let us calculate the generalized thermodynamic coordinates of the crystal. The entropy of a unit volume

$$S = -\left(\frac{\partial\Phi}{\partial T}\right)_{\text{total}} = -\frac{\partial\Phi}{\partial T} - \frac{\partial\Phi}{\partial\eta}\frac{\partial\eta}{\partial T}.$$

The second term is zero because of the equilibrium conditions (65.3), so that

$$S = -\frac{d\Phi_0}{dT} + R_b^{(0)} X_b - a\eta^2. \tag{65.13}$$

We find all the other thermodynamic coordinates similarly

$$x_b = R_b^{(0)}\Theta + M_{bd}^{(0)} X_d + K_b\eta + L_{bd} X_d \eta + Q_b \eta^2. \tag{65.14}$$

Now we can investigate the changes of the crystal properties, i.e. of the crystal's thermodynamic coefficients. The thermal capacity

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{\text{total}} = T\frac{\partial S}{\partial T} + T\frac{\partial S}{\partial \eta}\frac{\partial \eta}{\partial T}. \tag{65.15}$$

Substituting the expression (65.13) into (65.15), assuming $X_b = 0$ and using the relations (65.12) and (65.10) we obtain the thermal capacity C_p at constant, and, moreover, zero, mechanical stresses and an electric field:

$$C_p = \begin{cases} -T\dfrac{d^2\Phi_0}{dT^2} & \text{in the symmetric phase,} \\ -T\dfrac{d^2\Phi_0}{dT^2} + \dfrac{a^2T}{2B} & \text{in the dissymmetric phase.} \end{cases} \tag{65.16}$$

Thus under the transition from the symmetric to the dissymmetric modification thermal capacity increases jumpwise, the jump being equal to

$$\Delta C_p = \frac{a^2 T_c}{2B}. \tag{65.17}$$

This conclusion is based on the assumption of the absence of any singularities of the thermodynamic potential at the Curie point. In many transitions of the second kind it disagrees more or less with the experimental data; the degree of this disagreement is what shows the importance of the singularity experienced by the thermodynamic potential at the Curie point.

Pyroelectric coefficients $p_i = R_i$ and thermal expansion coefficients $\alpha_\lambda = R_{3+\lambda}$ are calculated with the aid of any of the following formulas

$$\begin{aligned} R_b &= \frac{\partial S}{\partial X_b} + \frac{\partial S}{\partial \eta}\frac{\partial \eta}{\partial x_b}, \\ R_b &= \frac{\partial x_b}{\partial T} + \frac{\partial x_b}{\partial \eta}\frac{\partial \eta}{\partial T}. \end{aligned} \tag{65.18}$$

The values of these coefficients in very weak electric fields and mechanical stresses are calculated in the same way as that used for the

derivation of formula (65.16); they are equal to

$$R_b = \begin{cases} R_b^{(0)} & \text{in the symmetric phase,} \\ R_b^{(0)} \pm \frac{K_b}{2}\sqrt{-\frac{a}{2B\Theta}} - \frac{aQ_b}{2B} & \text{in the dissymmetric phase.} \end{cases} \tag{65.19}$$

It follows from the properties of coefficients K_b and Q_b that those pyroelectric and thermal expansion coefficients which differ from zero in the symmetric phase experience in the transition to the dissymmetric phase a jump equal to

$$\Delta R_b = -\frac{aQ_b}{2B}. \tag{65.20}$$

These coefficients are the same in both types of domains.

On the contrary, those pyroelectric and thermal expansion coefficients (or their combinations) which differ from zero only in the dissymmetric phase, have opposite signs in different types of domains: as they approach the Curie point (from the dissymmetric phase) the coefficients increase, according to the law $|T - T_c|^{-1/2}$:

$$R_b = \pm\frac{K_b}{2}\sqrt{-\frac{a}{2B\Theta}}. \tag{65.21}$$

Let us, finally, consider the coefficients of dielectric permittivity $\varkappa_{ik} = 4\pi M_{ik}$ $(i, k = 1, 2, 3)$, the coefficients of elastic compliance, $s_{\lambda\mu} = M_{3+\lambda,\, 3+\mu}$ $(\lambda, \mu = 1, \ldots, 6)$, and the piezoelectric coefficients $d_{k\lambda} = M_{k,3+\lambda}$. They can all be calculated with the aid of either of the formulas:

$$\begin{aligned} M_{bd} &= \frac{\partial x_b}{\partial X_d} + \frac{\partial x_b}{\partial \eta}\frac{\partial \eta}{\partial X_d}, \\ M_{bd} &= \frac{\partial x_d}{\partial X_b} + \frac{\partial x_d}{\partial \eta}\frac{\partial \eta}{\partial X_b}. \end{aligned} \tag{65.22}$$

In very weak electric fields and at mechanical stresses they are

$$M_{bd} = \begin{cases} M_{bd}^{(0)} + \frac{K_b K_d}{2a\Theta} & \text{in the symmetric phase,} \\ M_{bd}^{(0)} + \frac{Q_b Q_d}{2B} - \frac{K_b K_d}{4a\Theta} \pm \\ \pm \frac{K_b Q_d + K_d Q_b}{2}\sqrt{-\frac{1}{2aB\Theta}} \pm \\ \pm L_{bd}\sqrt{-\frac{a\Theta}{2B}} & \text{in the dissymmetric phase.} \end{cases} \tag{65.23}$$

For the analysis of this expression we want to note first of all that the terms with radicals occur only in those coefficients M_{bd} (or their combinations) which differ from zero only in the dissymmet-

ric phase, while terms without radicals occur only in the coefficients that differ from zero even in the symmetric phase. Terms with products K_bK_d and Q_bQ_d correspond to different coefficients.

Thus, the coefficients M_{bd} differing from zero both in the symmetric and dissymmetric phases are identical in both types of domains. Three types of behaviour are possible for such coefficients.

1. The coefficient does not change under transition:

$$M_{bd} = M_{bd}^{(0)} \quad \text{in both phases.} \tag{65.24}$$

2. The coefficient jumps under transition

$$\Delta M_{bd} = \frac{Q_bQ_d}{2B}; \tag{65.25}$$

the jump of diagonal coefficients (such as $\varkappa_{11}$, s_{11} and s_{44}) being positive, i.e. in the dissymmetric phase the corresponding coefficient of dielectric permittivity or elastic compliance is larger than in the symmetric phase.

3. At the approach to the Curie point both from the dissymmetric and the symmetric phase the coefficient increases according to the law $|\Theta|^{-1}$. In this case near the Curie point the term $M_{bd}^{(0)}$ can be neglected, so that

$$M_{bd} = \begin{cases} \dfrac{K_bK_d}{2a\Theta} & \text{in the symmetric phase,} \\ -\dfrac{K_bK_d}{4a\Theta} & \text{in the dissymmetric phase.} \end{cases} \tag{65.26}$$

The sign of coefficient M_{bd} is not reversed after passing the Curie point; in particular, the diagonal coefficients remain positive, just as they should. Besides, there is a "law of doubling": at equal distances from the Curie point the coefficient M_{bd} in the symmetric phase is twice as large as in the dissymmetric phase.

Those coefficients M_{bd}, or their combinations, which differ from zero only in the dissymmetric phase are of equal absolute values but have opposite signs in the domains of different types. For such coefficients two types of behaviour are possible.

1. Coefficient M_{bd} increases in absolute value as $|\Theta|^{1/2}$ with the increase of the distance from the Curie point, but only when $K_bQ_d + K_dQ_b = 0$, and $L_{bd} \neq 0$. In this case

$$M_{bd} = \begin{cases} 0 & \text{in the symmetric phase,} \\ \pm L_{bd}\sqrt{-\dfrac{a\Theta}{2B}} & \text{in the dissymmetric phase.} \end{cases} \tag{65.27}$$

2. At the approach to the Curie point from the dissymmetric phase coefficient M_{bd} increases as $|\Theta|^{-1/2}$:

$$M_{bd} = \begin{cases} 0 & \text{in the symmetric phase,} \\ \mp \dfrac{K_b Q_d + K_d Q_b}{2} \sqrt{-\dfrac{1}{2aB\Theta}} & \text{in the dissymmetric phase.} \end{cases} \tag{65.28}$$

It is necessary for this that $K_b Q_d + K_d Q_b \neq 0$, and it makes no difference whether or not L_{bd} differs from zero.

Let us now consider the alteration of the thermodynamic coordinate x_b in a phase transition of the second kind. In the absence of electric field and mechanical stresses we obtain from (65.14)

$$x_b = \begin{cases} R_b^{(0)}\Theta & \text{in the symmetric phase,} \\ \left(R_b^{(0)} - \dfrac{aQ_b}{2B}\right)\Theta \pm K_b \sqrt{-\dfrac{a\Theta}{2B}} & \text{in the dissymmetric phase.} \end{cases} \tag{65.29}$$

(65.29) was derived on the assumption of thermal expansion and pyroelectric polarization being counted from the Curie temperature. The terms proportional to Θ are related to those components of thermal strain and pyroelectric polarization which differ from zero in both phases. They determine the jumps of the corresponding thermodynamic coefficients R_b.

Of an entirely different character are the spontaneous thermodynamic coordinates that differ from zero only in the dissymmetric phase: the components of spontaneous polarization and spontaneous strain

$$x_b^{(sp)} = \pm K_b \sqrt{-\frac{a\Theta}{2B}}. \tag{65.30}$$

They are zero in the symmetric phase, while in the dissymmetric one they rapidly (as $|\Theta|^{1/2}$) increase with the increase of the distance from the Curie point. The spontaneous thermodynamic coordinate is proportional to the dissymmetry parameter (cf. (65.6) and (65.30)), and therefore, when examining the transition under which this coordinate appears, it can be used as a dissymmetry parameter. Thus, in the study of ferroelectric transitions the spontaneous polarization is often used as the dissymmetry parameter. However, many phase transitions of the second kind are not accompanied by the appearance of spontaneuos coordinates, such are, e.g., transitions in quartz, sodium nitrate, brass, tungsten trioxide, Heyssler alloy.

An important class of phase transitions of the second kind are *ferroelectric transitions* in which spontaneous polarization appears*. This calls, in the crystallographic class of the ferroelectric phase for a larger number of the independent components of a matter vector than in the class of the paraelectric phase (in the ferroelectric transitions the symmetric phase is conventionally called *paraelectric*, and the dissymmetric phase is called *ferroelectric*). Therefore the ferroelectric phase is always related to one of the pyroelectric classes, the paraelectric phase usually belongs to one of the non-pyroelectric classes, although in principle the ferroelectric transition can connect, for instance, the modifications of classes $mm2$ and m, 2 and 1, m and 1.

In the only particular case of a twofold alteration of symmetry that we are considering here the ferroelectric transition is characterized by at least one of the coefficients K_i ($i = 1, 2, 3$) being nonzero. But in this case, as was shown above (see (65.26)), as the Curie point is approached, at least one of the components of the tensor of dielectric permittivity increases as $|\Theta|^{-1}$ increasing in the paraelectric phase twice as rapidly as in the ferroelectric phase:

$$\varkappa_{ij} = \begin{cases} \dfrac{2\pi K_i K_j}{\alpha\Theta} & \text{in the paraelectric phase,} \\ -\dfrac{\pi K_i K_j}{\Theta a} & \text{in the ferroelectric phase} \\ & (i, j = 1, 2, 3). \end{cases} \tag{65.31}$$

The ferroelectric transitions are also characterized by the appearance in the ferroelectric phase of piezoelectric coefficients which increase as $|\Theta|^{-1/2}$ with the approach to the Curie point. Such are the piezoelectric coefficients

$$d_{i\lambda} = \begin{cases} 0 & \text{in the paraelectric phase,} \\ \mp \dfrac{K_i Q_{3+\lambda}}{2} \sqrt{-\dfrac{1}{2aB\Theta}} & \text{in the ferroelectric phase} \\ & (i = 1, 2, 3;\ \lambda = 1, \ldots, 6). \end{cases} \tag{65.32}$$

At least three of them differ from zero, since the coefficients Q_4, Q_5 and Q_6 do not vanish in any of the crystallographic classes.

Such are the properties common in all ferroelectrics. Table 65.1 shows how they are displayed in ferroelectric crystals.

Along with spontaneous polarization in some ferroelectric transitions a spontaneous strain develops for instance in transitions in potassium dihydrophosphate and in Rochelle salt. Here, along

* For information on ferroelectrics see Känzig (1957, 1970); Jona, Shirane (1962); Smolensky and Krainik (1968); Barfoot (1970); Zheludev (1968, 1973 and 1976); Sonin and Strukov (1970); Smolensky, Bokov, Isupov et al. (1971); Vaks (1973). In particular, on the symmetry of crystal modifications associated with ferroelectric transitions see Zheludev and Shuvalov (1956); Sonin and Zheludev (1959); Indenbohm (1960a); Shuvalov (1963 and 1970); Levanyuk and Sannikov (1971); Sonin (1976).

Table 65.1

Alterations of the Physical Properties of Crystals in Some Phase Transitions of the Second Kind

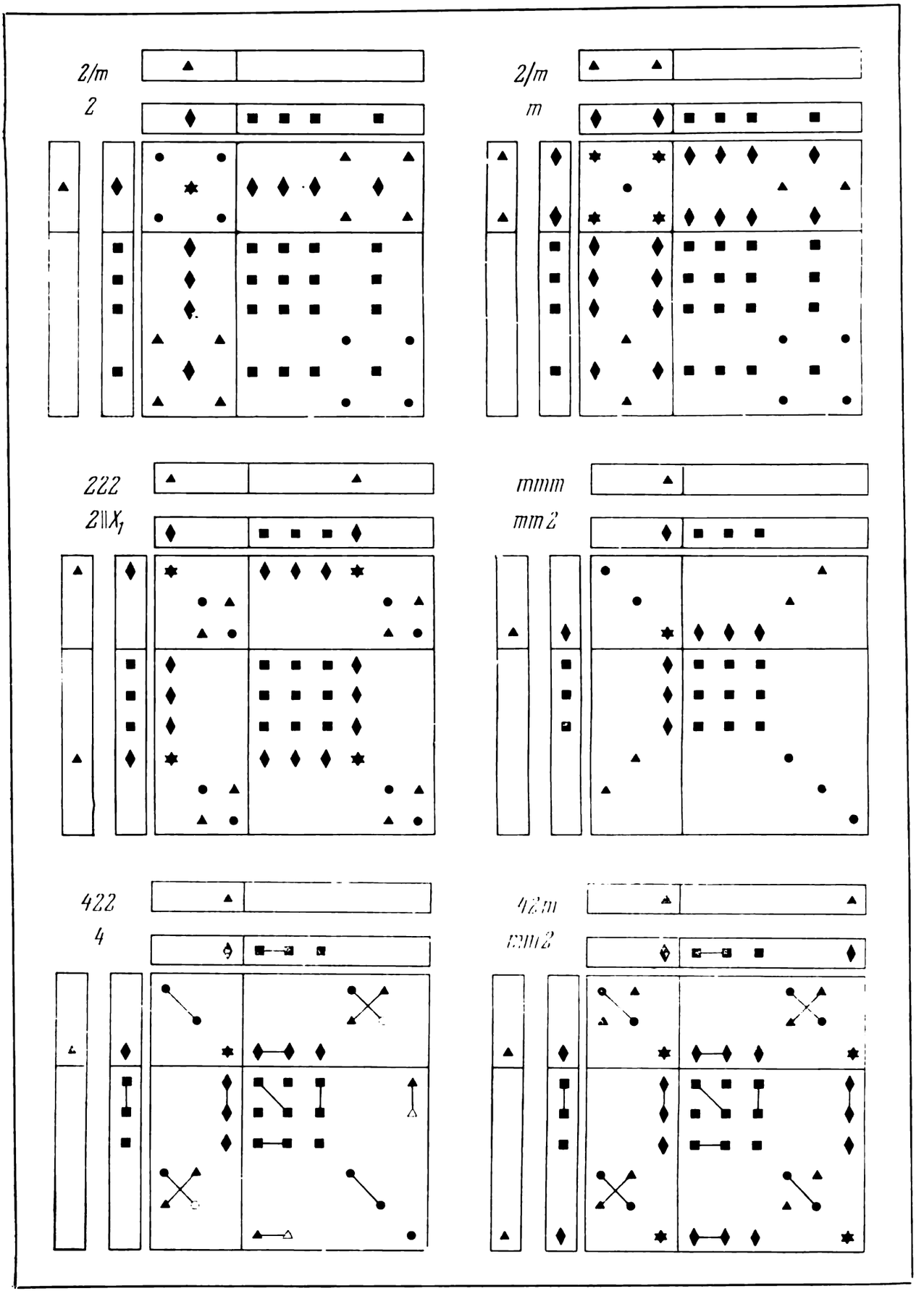
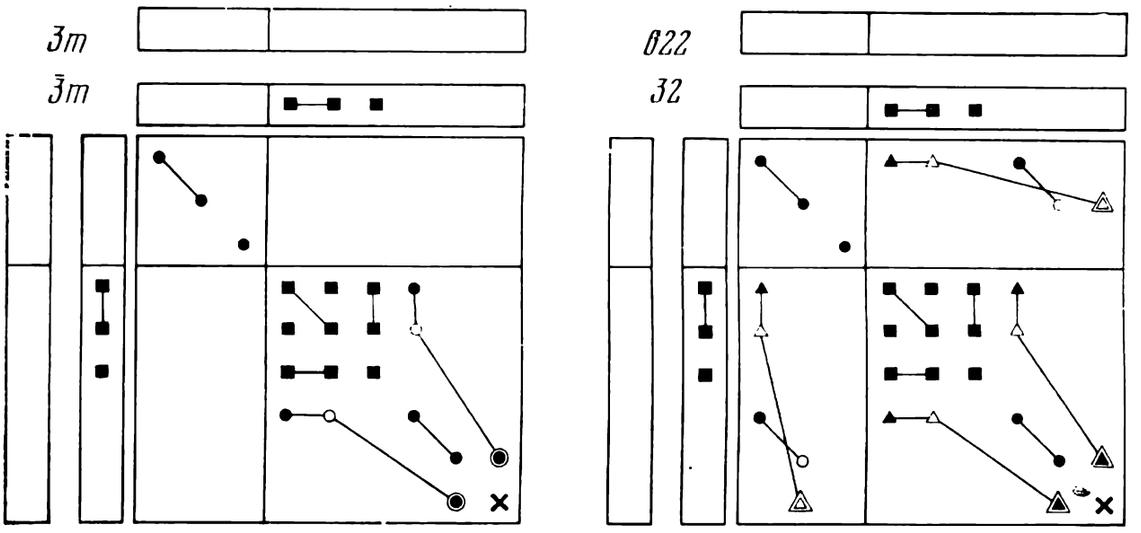
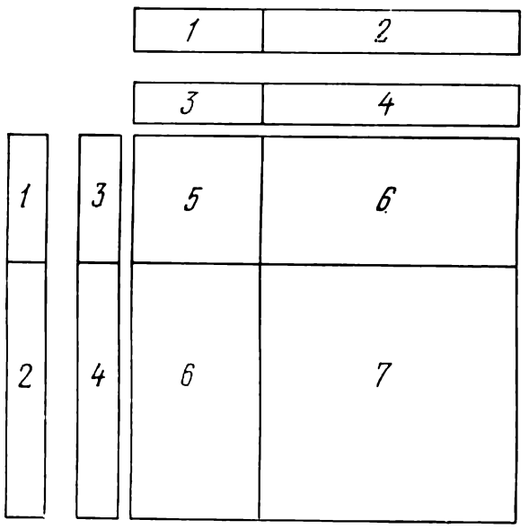


Table 65.1 (Cont'd)



Notation



Quantity	In symmetric phase	In dissymmetric phase
▲	zero	$\sim \sqrt{\lvert\theta\rvert}$
♦	zero	$\sim \frac{1}{\sqrt{\lvert\theta\rvert}}$
✱	$\sim \frac{2}{\lvert\theta\rvert}$	$\sim \frac{1}{\lvert\theta\rvert}$
■	jumps under transition differs from zero, does not experience a jump	
●		

1—spontaneous polarization, *2* — spontaneous deformation, *3*—pyroelectric coefficients, *4*—thermal expansion coefficients, *5*—dielectric permittivity coefficients, *6*—piezoelectric coefficients, *7*—elastic compliance coefficients. Other notation is the same as in Table 58.5. All schemes are symmetric with respect to the principal diagonal.

with one of the coefficients K_i ($i = 1, 2, 3$), one of the coefficients $K_{3+\lambda}$ ($\lambda = 1, \ldots, 6$) also differs from zero. In the domains of different types both the spontaneous polarization and the spontaneous strain have opposite signs; hence the sign of spontaneous strain is defined by the sign of spontaneous polarization, as shown in Fig. 65.2. With the approach to the Curie point under these transitions not only the dielectric permittivity coefficient, but also one of the elastic

compliance coefficients increased as $|\Theta|^{-1}$

$$s_{\lambda\mu} = \begin{cases} \dfrac{K_{3+\lambda}K_{3+\mu}}{2a\Theta} & \text{in the paraelectric phase,} \\ -\dfrac{K_{3+\lambda}K_{3+\mu}}{4a\Theta} & \text{in the ferroelectric phase} \end{cases} \tag{65.33}$$

and one of the piezoelectric coefficients

$$d_{i\lambda} = \begin{cases} \dfrac{K_i K_{3+\lambda}}{2a\Theta} & \text{in the paraelectric phase,} \\ -\dfrac{K_i K_{3+\lambda}}{4a\Theta} & \text{in the ferroelectric phase.} \end{cases} \tag{65.34}$$

Moreover, some elastic com iance coefficients that differ from zero only in the ferroelectric phase increase as $|\Theta|^{-1/2}$ with the approach to the Curie point

$$s_{\lambda\mu} = \begin{cases} 0 & \text{in the paraelectric phase,} \\ \mp \dfrac{K_{3+\lambda}Q_{3+\mu} + K_{3+\mu}Q_{3+\lambda}}{2} \sqrt{-\dfrac{1}{2aB\Theta}} & \text{in the ferroelectric phase.} \end{cases} \tag{65.35}$$

These distinctive features of the ferroelectric transitions in Rochelle salt and potassium dihydrophosphate are also shown in Table 65.1.

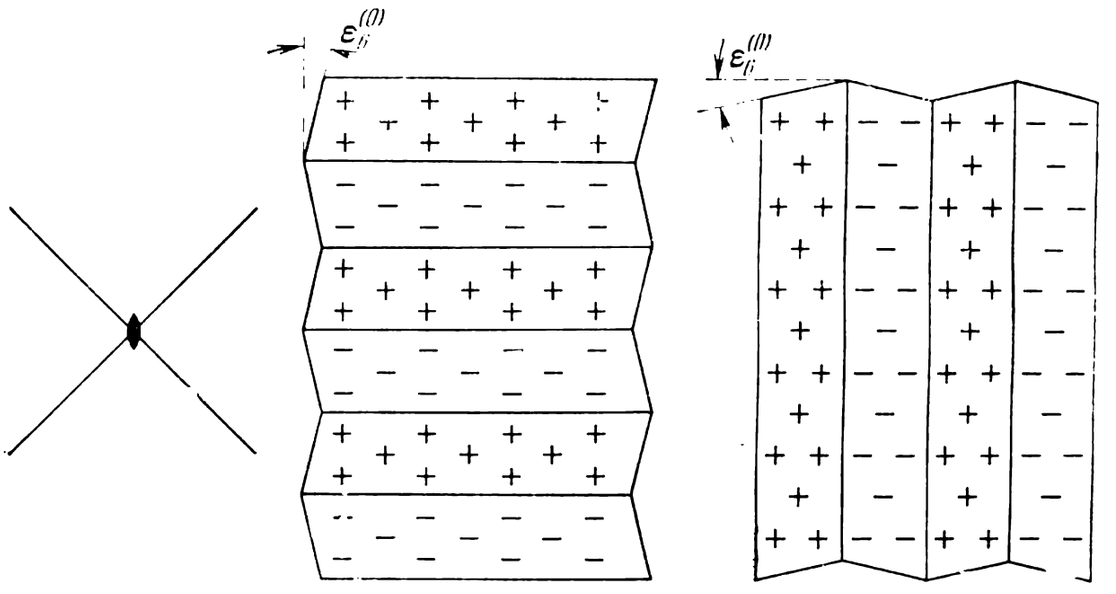


Fig. 65.2. Spontaneous polarization and spontaneous deformation of domains of the ferroelectric modification ($mm2$) of potassium dihydrophosphate. The orientation of the symmetry elements is shown on the left. Spontaneous deformation ε_6^0 is exaggerated

The range of differences between the phases will increase still more if we also include in our considerations the ferroelectric transitions accompanied by greater than twofold alterations of symmetry (e.g. the ferroelectric transition in barium titanate). However, against

the background of these differences the common properties of all ferroelectric transitions become all the more apparent. Among these properties we include the development of spontaneous polarization; the increase, as $|T - T_c|^{-1}$, of one of the dielectric permittivity coefficients with the approach to the Curie point both from the ferroelectric and the paraelectric side, the law of doubling being obeyed, the presence of piezoelectric properties in the ferroelectric modification, some piezoelectric coefficients attaining very high values near the Curie point.

Various technological uses of ferroelectrics are based on the anomalously high values of dielectric permittivity and piezoelectric coefficients.

Physical properties of crystals display less important anomalies in many phase transitions of the second kind than in the ferroelectric transitions. Thus, in the α-β transition in quartz investigated by I. A. Yakovlev (1957), no thermodynamic coefficients attain unusually high values; in the dissymmetric phase (class 32) there appear one new elastic compliance coefficient and one piezoelectric coefficient which increase as $|\Theta|^{-1/2}$ with the decrease of temperature (Table 65.1).

In the phase transitions in sodium nitrate (see Table 64.1), whose theory was suggested by Dzyaloshinsky and Lifshits (1957), the length of an elementary translation in the direction of the principal axis is doubled, while the point group remains unaltered. In such transitions only one type of changing thermodynamic coefficients is possible—the jumps of some of them. This is corroborated by Table 65.1. A simple calculation shows that the jumps of the thermal expansion and elastic compliance coefficients are connected in this case by the relations

$$\frac{\Delta\alpha_1}{\Delta\alpha_3} = \frac{\Delta s_{11}}{\Delta s_{13}} = \frac{\Delta s_{12}}{\Delta s_{13}} = \frac{\Delta s_{13}}{\Delta s_{33}} = \frac{Q_1}{Q_3}. \tag{65.36}$$

The thermal expansion of sodium nitrate is highly anisotropic: $\alpha_1 \approx 0.1\alpha_3$. Dzyaloshinsky and Lifshits assumed that the jumps of these quantities are also connected by approximately the same relation. Then the experimental results of Cornfeld and Chudinov (1957) become quite conceivable: they revealed the jump of the coefficient s_{33}, but observed no jumps of s_{11} and s_{12}.

Sec. 66. Mathematical Methods of the Theory of Phase Transitions

As was noted in Sec. 64, when two crystal modifications are connected by a phase transition of the second kind, the space group G_D of one of them is found to be a subgroup of the space group G of the other: $G_D \subset G$. However, this is only a necessary but not at all a sufficient condition; an important place in the fundamental works on the theory of phase transitions is occupied by the ascertain-

ing of other conditions that must be satisfied by the symmetry groups of crystal modifications connected by a phase transition of the second kind (Landau, 1937; Lifshits, 1941; Landau and Lifshits, 1976); this involves the use of rather a complicated mathematical apparatus, primarily the theory of group representation.* Group G of the symmetric modification can be conveniently considered as the specified one, while groups G_D of the dissymmetric modifications which can be connected with the symmetric one by a phase transition of the second kind, are to be found.

For this purpose we introduce a microscopic function of crystal density $\rho(x_1, x_2, x_3)$ at the phase transition point, it is invariant, with respect to the space group G. In the dissymmetric modification the function of density is $\rho + \delta\rho$, $\delta\rho$ being invariant only with respect to group G_D, but not with respect to G. With function $\delta\rho$ it is possible to construct real linearly independent and in some way normalized functions, $\varphi_\alpha^{(m)}$ $(\alpha = 1, \ldots, n_m)$ such that, on the one hand, each of them is transformed in accordance with a certain physically irreducible** representation Γ_m of dimension n_m of group G, and on the other hand, such that $\delta\rho$ is represented as a linear combination

$$\delta\rho = \sum_m \sum_\alpha c_\alpha^{(m)} \varphi_\alpha^{(m)}. \tag{66.1}$$

At the very transition point all coefficients $c_\alpha^{(m)}$ are zero, while in the dissymmetric modification at least one coefficient, corresponding to a non-unit representation, differs from zero, for otherwise the symmetry would not alter in the transition. Thus, among the irreducible representations whose base functions are contained in expansion (66.1) there is at least one which is non-unit.

The coefficients $c_\alpha^{(m)}$ which correspond to non-unit representations, characterize the value of terms not invariant with respect to group G in the expression of the density function of the dissymmetric phase (66.1) and thus play the role of a multicomponent parameter of dissymmetry. They depend on external conditions; to be definite, we shall consider that the latter are specified by the generalized thermodynamic forces T and $\mathbf{X} = (X_1, \ldots, X_9)$. In the theory of phase transitions of the second kind it is convenient to regard, temporarily, the thermodynamic potential Φ of the dissymmetric modification as a function of not only thermodynamic forces, but also of the components of the parameter of dissymmetry $\boldsymbol{c}$, and then to proceed finding the latter as functions of temperature, $c_\alpha^{(m)} = c_\alpha^{(m)}(T)$, from the conditions

$$\left(\frac{\partial \Phi(T, X; \boldsymbol{c})}{\partial c_\alpha^{(m)}} \right)_{X=0} = 0. \tag{66.2}$$

Equations (66.2) follow from the minimality of the thermodynamic potential Φ at fixed thermodynamic forces. For the same reason matrix

$$\left\| \left(\frac{\partial^2 \Phi(T, X, \boldsymbol{c})}{\partial c_\alpha^{(m)} \partial c_\beta^{(l)}} \right)_{X=0} \right\|$$

is positively definite.

It was explained in Sec. 65 that the thermodynamic potential of the dissymmetric phase must be invariant with respect to the space group G of the symmetric phase, and therefore its dependence on the coefficients $c_\alpha^{(m)}$ is actually the

* The reader is supposed to be familiar with the theory of space group representation, see Landau and Lifshits (1974 and 1976); Petrashen' and Trifonov (1967); Streitwolff (1971); Beer and Pikus (1972).

** We call physically irreducible a real irreducible representation or a sum of two complex-conjugate non-real irreducible representations.

dependence on the invariants composed of these coefficients. In the immediate vicinity of the transition point the $c_\alpha^{(m)}$ are small, and the main role is played by the invariants of the lowest degrees. Generally, the number of linearly independent invariants of degree s, which can be composed of the components of a quantity transformed according to any representation B of the group G, is equal to the number of unit representations contained in the representation $[B^s]$, i.e. to the symmetric power s of representation B. This number

$$m_G(B,s) = \frac{1}{N(G)} \sum_{g \in G} [\chi_B^s](g), \tag{66.3}$$

where $N(G)$ is the order of the group G, $[\chi_\beta^s]$ is the symmetric s-th power of the character of representation B. However, linear invariants cannot be composed of quantities transformed according to a physically irreducible representation; also, each such representation has only one quadratic invariant which, with a corresponding choice of basis $\varphi_1^{(m)}, \ldots, \varphi_n^{(m)}$, can be represented as a sum of the squares of the components. Thus, on the assumption of the permissibility of expanding the thermodynamic potential in a series of the components of the dissymmetry parameter, we obtain the beginning of this expansion in the form

$$\Phi = \Phi_0 + \sum_m A^{(m)} \sum_{\alpha=1}^{n_m} (c_\alpha^{(m)})^2 + \ldots,$$

where $A^{(m)} = A^{(m)}(T, X)$ are functions of the thermodynamic forces.

In the symmetric modification the thermodynamic potential must be at its minimum when all the $c_\alpha^{(m)}$ are zero, while in the dissymmetric modification this must be the case when at least some of them differ from zero. Since the sums of squares are essentially positive, the first condition is satisfied when all $A^{(m)}$ are positive, and the second one—when at least some of them are negative. Evidently, the latter vanish at the transition point. But since it is physically impossible that without a particular reason several independent functions $A^{(m)}(T, X)$ would vanish in exactly the same conditions $T = T_c$, $X = 0$, it is natural to expect that only one of them would become zero, and that the transition would be connected with the only physically irreducible representation Γ, with the one for which the coefficient A becomes zero. The components c_α of the dissymmetry parameter which characterize the given transition are transformed according to this representation. Correspondingly, the alteration of the density function (66.1) can be written in the form

$$\delta\rho = \sum_{\alpha=1}^{n} c_\alpha \varphi_\alpha; \tag{66.4}$$

in conditions (66.2) the superscripts m can also be omitted.

The combination of cubic invariants of the parameter of dissymmetry would seem to be the first non-vanishing term in the expansion of the thermodynamic potential. However, third-degree invariants are essentially alternating, therefore they must be absent for the thermodynamic potential to be at its minimum value at the transition point. Since, on the other hand, there are no reasons to expect that the coefficients of these invariants would vanish at exactly the same temperature at which the coefficient A becomes zero, it remains to demand that the representation Γ would not admit the existence of third-degree invariants at all, i.e. that according to (66.3) it would satisfy the condition

$$\sum_{g \in G} [\chi_\Gamma^3](g) = 0. \tag{66.5}$$

It was introduced by Landau (1937).

Thus, the expansion of the thermodynamic potential acquires the form

$$\Phi = \Phi_0 + A \sum_{\alpha=1}^{n} (c_\alpha)^2 + \sum_i B_i f_i^{(4)}(c) + \dots, \tag{66.6}$$

where $f_i^{(4)}(c)$ are the fourth-degree linearly independent invariants composed of the components of the dissymmetry parameter, and B_i are certain functions of the generalized thermodynamic forces, which are at the first approximation believed to be constants (cf. expansions (65.1) and (65.7)).

The demands on the representation Γ, in accordance with which the dissymmetry parameter could transform, are not restricted to Landau condition (66.5). The point is that in reality the irreducible representations of space groups are enumerated by a continuous parameter which is the vector $\boldsymbol{k}$ of the first Brillouin zone of the reciprocal lattice, and only in the case when several irreducible representations correspond to one vector $\boldsymbol{k}$ they are enumerated by m too. Therefore the coefficients $A = A(\boldsymbol{k}, T, X)$. Assuming that A are sufficiently smooth functions of the vector $\boldsymbol{k}$, we have

$$A(\boldsymbol{k}_0 + \delta\boldsymbol{k}) = A(\boldsymbol{k}_0) + \frac{\partial A(\boldsymbol{k}_0)}{\partial \boldsymbol{k}} \cdot \delta\boldsymbol{k} + \frac{1}{2} \frac{\partial^2 A(\boldsymbol{k}_0)}{\partial \boldsymbol{k}\, \partial \boldsymbol{k}} : \delta\boldsymbol{k}\, \delta\boldsymbol{k} + \dots. \tag{66.7}$$

Let the transition be connected with the representation $\Gamma(\boldsymbol{k}_0)$. Then in the symmetric modification all $A(\boldsymbol{k}_0 + \delta\boldsymbol{k})$ from a certain vicinity of the vector $\boldsymbol{k}_0$ are positive; with the approach of temperature to the Curie point they are diminished and, finally, at the very transition point $A(\boldsymbol{k}_0)$ vanishes while quantities $A(\boldsymbol{k}_0 + \delta\boldsymbol{k})$ are still positive. But for this it is necessary that at $\boldsymbol{k} = \boldsymbol{k}_0$ the function $A(\boldsymbol{k})$ would have a minimum, i.e. that there would be no linear terms in (66.7) and that the quadratic ones would be positive. The derivative $\partial A/\partial \boldsymbol{k}$ can vanish at $\boldsymbol{k} = \boldsymbol{k}_0$ because of the symmetry vector $\boldsymbol{k}_0$. As a matter of fact this derivative is a vector invariant with respect to the point group of symmetry $H(\boldsymbol{k}_0)$ of vector $\boldsymbol{k}_0$. If this group does not leave a single direction invariant, i.e. belongs to the 22 non-pyroelectric crystallographic point groups, the derivative $\partial A/\partial \boldsymbol{k}$ will inevitably become zero at $\boldsymbol{k} = \boldsymbol{k}_0$. Another imaginable case, when the simultaneous vanishing of $A(\boldsymbol{k}_0)$ and $\partial A(\boldsymbol{k}_0)/\partial \boldsymbol{k}$ is caused not by the symmetry of vector $\boldsymbol{k}_0$ but by special properties of the function $A(\boldsymbol{k})$, is not to be considered, because in this case $\boldsymbol{k}_0$ will continuously change with the alteration of the external conditions (e.g. pressure), i.e. the dissymmetric phase will not be a crystal. Thus, the physically irreducible representation $\Gamma(\boldsymbol{k})$ connected with the phase transition of the second kind must be characterized by vector $\boldsymbol{k}$ with the non-pyroelectric symmetry group $H(\boldsymbol{k})$. In this case because the representation $\Gamma(\boldsymbol{k})$ is real it follows that the star of the vector $\boldsymbol{k}$ should also include the vector $-\boldsymbol{k}$, even if it is not called for by the crystal symmetry, this meaning that in the determination of group $H(\boldsymbol{k})$ the crystallographic class of the crystal should be replaced by its Laue class (i.e. if the crystal is not centrosymmetric, a centre of symmetry must be added to its symmetry elements).

The described condition was introduced by E. M. Lifshits (1941) as a consequence of a more general condition, and we shall therefore call it the milder Lifshits condition *.

Dzyaloshinsky remarked (1964) that it would be more correct to demand the identical equality to zero of the term linear with respect to $\delta\boldsymbol{k}$ in the expansion of the thermodynamic potential into powers of $\delta\boldsymbol{k}$, and in this expansion, along

* In the description of the principle use has been made of the work of Dzyaloshinsky (1964). Khachaturyan (1965) arrived at the same conclusion, though on the basis of somewhat different considerations.

with terms

$$\delta k \cdot \frac{\partial A(k_0)}{\partial k} \sum_{\alpha} (c_\alpha)^2,$$

previously considered can—if the representation $\Gamma(k_0)$ is not one-dimensional—be included still another term

$$\delta k \cdot v(c_1, \ldots, c_n),$$

where v is a quantity quadratic with respect to the components c_i and transforming as a vector under all transformations from group G_{k_0}. Therefore the representation $\Gamma(k)$ must satisfy the condition

$$\sum_{g \in G_k} \chi_V(g) [\chi_\Gamma^2](g) = 0, \tag{66.8}$$

which determines the absence of terms linear with respect to δk and quadratic with respect to c_α in the expansion of the thermodynamic potential. (66.3) has been used here; χ_V is the character of the vector representation, $[\chi_\Gamma^2]$ is the symmetric square of the character of representation Γ. Condition (66.8) could be naturally called the Dzyaloshinsky condition; it is somewhat stronger than the milder Lifshits condition.

The general Lifshits condition demands that the components c_α of the parameter of dissymmetry would not depend on the space coordinates. Therefore it is necessary for the thermodynamic potential Φ, regarded as a function of $\partial c_\alpha / \partial x_i$, to be at its minimum at $\partial c_\alpha / \partial x_i = 0$. The corresponding expansion looks as

$$\Phi = \Phi_0 + \sum_{\alpha, i} a_{\alpha i} \frac{\partial c_\alpha}{\partial x_i} + \sum_{\alpha, \beta, i} b_{\alpha\beta i} \left(c_\alpha \frac{\partial c_\beta}{\partial x_i} + c_\beta \frac{\partial c_\alpha}{\partial x_i} \right) + \\ + \sum_{\alpha, \beta, i} d_{\alpha\beta i} \left(c_\alpha \frac{\partial c_\beta}{\partial x_i} - c_\beta \frac{\partial c_\alpha}{\partial x_i} \right) + \ldots, \tag{66.9}$$

where $a_{\alpha i}$, $b_{\alpha\beta i}$, $d_{\alpha\beta i}$ are constant coefficients, the set $b_{\alpha\beta i}$ being symmetric and $d_{\alpha\beta i}$ antisymmetric with respect to the permutation of subscripts α and β. Having considered the thermodynamic potential of the whole crystal, i.e. the integral $\int \Phi \, dV$, we arrive at the conclusion that only the last term of expansion (66.9) is essential, since upon the application of the Gauss-Ostrogradsky theorem all the other terms will come to surface integrals of c_α and $c_\alpha c_\beta$. Thus the vanishing of this term must follow from the properties of representation Γ. Coefficients $d_{\alpha\beta i}$ transform according to the representation $V\{\Gamma^2\}$ which is the product of the vector representation V of group G and the antisymmetric square $\{\Gamma^2\}$ of representation Γ. On the other hand, since $d_{\alpha\beta i}$ are included in the expansion of the thermodynamic potential, they must be invariant with respect to group G. The number of such invariants is equal to the number of unit representations in the generally reducible representation $V\{\Gamma^2\}$ and this number must be zero to make transition possible:

$$\sum_{g \in G} \chi_V(g) \{\chi_\Gamma^2\}(g) = 0. \tag{66.10}$$

(66.3) has been used here; χ_V is the character of the vector representation of group G, $\{\chi_\Gamma^2\}$ is the antisymmetric square of the character of representation Γ. It is the equality (66.10) that states the general Lifshits condition, the milder Lifshits condition is its consequence, see Lifshits (1941), Landau and Lifshits (1964).

(66.8) and (66.10) can be considered to be the amplifications of the milder Lifshits condition; the latter is one of the cornerstones of the theory, which greatly determines the character of its mathematical apparatus. The vectors $\boldsymbol{k}$ satisfying this condition are zero, either a half, a third or a quarter of one of the reciprocal lattice vectors. In the first case, examined in detail by Indenbohm (1960), the group of translations T of the symmetric phase is included in the kernel of the homomorphism of the representation Γ, so that the latter is found to be the representation of the point group of the symmetric modification; in this case the translation symmetry of the crystal does not change at all. In all other cases the homomorphism kernel of the representation Γ includes, even though not the translation group itself, its subgroup $T_{\{k\}}$ of a comparatively small index; it consists of all translations $\boldsymbol{t} \in T$ for which $\boldsymbol{t}\cdot\boldsymbol{k}$ is zero or an integer at all $\boldsymbol{k}$ of the star $\{\boldsymbol{k}\}$. Representation Γ is again found to be the representation of a group of a finite order, the latter being not larger than the product of the order of the symmetric phase point group and index $T_{\{k\}}$ with respect to T. This contingency allows to formulate the properties of representation Γ of the infinite group G in the language of the theory of finite groups.

If the star $\{\boldsymbol{k}\}$ contains several vectors, then the translation groups characterizing the possible Bravais lattices of low-symmetry phases can be generated not by all vectors $\boldsymbol{k}_1 \ldots, \boldsymbol{k}_q$ included in the star, but by one of them (for example, T_{k_1}), by a pair of vectors ($T_{k_1k_2}$, $T_{k_1k_3}$, etc.), . . ., by a set of $q-1$ vectors. In distinction from groups $T_{\{k\}}$ describing the Bravais lattices of the same system with the initial one, to these groups there correspond the Bravais lattices of lower systems.

All possible changes of the Bravais lattice of a crystal were listed by Lifshits (1941); they are given in Table 66.1. It should be borne in mind, when using this Table, that along with the crystal translation symmetry the rotation symmetry can also be lowered, while the lattice will correspondngly be slightly deformed; this contingency is not shown in the Table, the Bravais lattices being referred in it to the most symmetric system of those to which they can be generally referred. Anyway whatever is the true symmetry of the resulting lattice, it will contain those and only those points which are given in the Table.

In the first and second columns of Table 66.1 are shown the Bravais lattices of the symmetric and dissymmetric modifications respectively. In the third column the latter modification is specified with the aid of base vectors $\boldsymbol{a}_i$ of the symmetric phase primitive lattice, the base-centred cell of the initial phase is specified by vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, and $1/2\ (\boldsymbol{a}_1 + \boldsymbol{a}_2)$; the face-centred cell, by vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$; $1/2\ (\boldsymbol{a}_2 + \boldsymbol{a}_3)$, $1/2\ (\boldsymbol{a}_3 + \boldsymbol{a}_1)$, $1/2\ (\boldsymbol{a}_1 + \boldsymbol{a}_2)$; the body-centred cell, by vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, $1/2\ (\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3)$; in the rhombohedral lattice vectors $\boldsymbol{a}_i$ are chosen along the edges of an elementary rhombohedron. The fourth column shows how many times the number of atoms in a unit cell is increased under a transition, or, which is just the same, how many times the translation symmetry is reduced; we shall denote this number by N_t.

Table 66.1 shows that the lattice spacings are doubled in the majority of cases, some spacings in body-centred and face-centred lattices can be quadrupled, and in a hexagonal lattice,—tripled. The cell volume can change $N_t = 2, 3, 4, 6, 8, 16$ and 32 times. It should be remembered that there are possible (and very widespread) transitions under which the translation symmetry does not change at all (see Sec. 64).

Let us return to the analysis of representation Γ. As was already noted, group $T_{\{k\}}$ is included in the kernel of the homomorphism G_Γ of this representation,

Alterations of the Bravais Lattice under Transitions of the Second Kind

$P\bar{1}$	$P\bar{1}$	$2a_1,\ a_2,\ a_3$	2
$P2/m$	$P2/m$	$2a_1,\ a_2,\ a_3$	2
	$P2/m$	$a_1,\ 2a_2,\ a_3$	2
	$C2/m$	$2a_1,\ 2a_2,\ a_3;\ a_1+a_2$	2
$C2/m$	$C2/m$	$a_1,\ a_2,\ 2a_3;\ a_1+a_2$	2
	$P2/m$	$a_1,\ a_2,\ a_3$	2
	$P\bar{1}$	$a_1+a_2,\ \frac{1}{2}(a_1-a_2),\ a_3$	2
	$C2/m$	$2a_1,\ 2a_2,\ a_3;\ a_1+a_2$	4
$Pmmm$	$Pmmm$	$2a_1,\ a_2,\ a_3$	2
	$Cmmm$	$2a_1,\ 2a_2,\ a_3;\ a_1+a_2$	2
	$Fmmm$	$2a_1,\ 2a_2,\ 2a_3;\ a_2+a_3,\ a_3+a_1,\ a_1+a_2$	2
$Cmmm$	$Cmmm$	$a_1,\ a_2,\ 2a_3;\ \frac{1}{2}(a_1+a_2)$	2
	$Pmmm$	$a_1,\ a_2,\ a_3$	2
	$Immm$	$a_1,\ a_2,\ 2a_3;\ \frac{1}{2}(a_1+a_2+2a_3)$	2
	$P2/m$	$a_1,\ a_1+a_2,\ \frac{1}{2}(a_1-a_2)$	2
	$C2/m$	$2a_1,\ 2a_3,\ \frac{1}{2}(a_1+a_2);\ a_1+a_3$	2
	$Cmmm$	$2a_1,\ 2a_2,\ a_3;\ a_1+a_2$	4
	$Fmmm$	$2a_1,\ 2a_2,\ 2a_3;\ a_2+a_3,\ a_3+a_1,\ a_1+a_2$	4
$Fmmm$	$Cmmm$	$a_1,\ a_2,\ a_3;\ a_1+a_2$	2
	$P\bar{1}$	$\frac{1}{2}(a_1+a_2),\ \frac{1}{2}(a_1+a_3),\ a_2+a_3$	2
	$C2/m$	$2a_1,\ 2a_2,\ \frac{1}{2}(a_1+a_3);\ a_1+a_2$	4
	$Fmmm$	$2a_1,\ 2a_2,\ 2a_3;\ a_2+a_3,\ a_3+a_1,\ a_1+a_2$	8
$Immm$	$Pmmm$	$a_1,\ a_2,\ a_3$	2
	$C2/m$	$2a_1,\ 2a_2,\ \frac{1}{2}(a_1+a_2+a_3);\ a_1+a_2$	2
	$Cmmm$	$2a_1,\ 2a_2,\ a_3;\ a_1+a_2$	4
	$Fmmm$	$2a_1,\ 2a_2,\ 2a_3;\ a_2+a_3,\ a_3+a_1,\ a_1+a_2$	4
$P4/mmm$	$P4/mmm$	$a_1,\ a_2,\ 2a_3$	2
	$P4/mmm$	$a_1+a_2,\ a_1-a_2,\ a_3$	2
	$I4/mmm$	$a_1+a_2,\ a_1-a_2,\ 2a_3;\ a_1+a_3$	2
	$Pmmm$	$2a_1,\ a_2,\ a_3$	2
	$Cmmm$	$2a_1,\ 2a_3,\ a_2;\ a_1+a_3$	2
	$P4/mmm$	$2a_1,\ 2a_2,\ a_3$	4
	$I4/mmm$	$2a_1,\ 2a_2,\ 2a_3;\ a_1+a_2+a_3$	4
$I4/mmm$	$P4/mmm$	$a_1,\ a_2,\ a_3$	2
	$Cmmm$	$a_1+a_2,\ a_3,\ a_1-a_2;\ \frac{1}{2}(a_1+a_2+a_3)$	2
	$C2/m$	$a_1,\ a_2+a_3,\ a_2-a_3;\ \frac{1}{2}(a_1+a_2+a_3)$	2
	$P4/mmm$	$a_1+a_2,\ a_1-a_2,\ a_3$	4
	$Cmmm$	$2a_1,\ 2a_3,\ a_2;\ a_1+a_3$	4
	$P2/m$	$2a_1,\ 2a_2,\ \frac{1}{2}(a_1+a_2+a_3)$	4
	$I4/mmm$	$a_1+a_2,\ a_1-a_2,\ 2a_3;\ a_1+a_3$	4
	$I4/mmm$	$2a_1\ 2a_2,\ 2a_3;\ a_1+a_2+a_3$	8
$Pm3m$	$P4/mmm$	$a_1,\ a_2,\ 2a_3$	2
	$P4/mmm$	$a_1+a_2,\ a_1-a_2,\ a_3$	2
	$Fm3m$	$2a_1,\ 2a_2,\ 2a_3;\ a_2+a_3,\ a_3+a_1,\ a_1+a_2$	2
	$P4/mmm$	$2a_1,\ 2a_2,\ a_3$	4
	$Im3m$	$2a_1,\ 2a_2,\ 2a_3;\ a_1+a_2+a_3$	4
	$Pm3m$	$2a_1,\ 2a_2,\ 2a_3$	8

Table 66.1 (cont'd)

$Im3m$	$Pm3m$	$a_1,\ a_2,\ a_3$	2
	$Cmmm$	$a_1,\ a_2+a_3,\ a_2-a_3;\ {}^1/_2\ (a_1+a_2+a_3)$	2
	$P4/mmm$	$a_1+a_2,\ a_1-a_2,\ a_3$	4
	$P2/m$	$2a_1,\ 2a_2,\ {}^1/_2\ (a_1+a_2+a_3)$	4
	$Fm3m$	$2a_1,\ 2a_2,\ 2a_3;\ a_2+a_3,\ a_3+a_1,\ a_1+a_2$	4
	$Im3m$	$2a_1,\ 2a_2,\ 2a_3;\ a_1+a_2+a_3$	8
$Fm3m$	$P4/mmm$	${}^1/_2\ (a_1+a_2),\ {}^1/_2\ (a_1-a_2),\ a_3$	2
	$R\bar{3}m$	$a_1+{}^1/_2\,(a_2+a_3),\ a_2+{}^1/_2\,(a_3+a_1),$ $a_3+{}^1/_2\,(a_1+a_2)$	2
	$Pm3m$	$a_1,\ a_2,\ a_3$	4
	$P2/m$	$a_1+a_2,\ a_1-a_2,\ {}^1/_2\,(a_1+a_3)$	4
	$I4/mmm$	$a_1,\ a_2,\ 2a_3;\ a_3+{}^1/_2\,(a_1+a_2)$	4
	$Fm3m$	$2a_1,\ 2a_2,\ 2a_3;\ a_2+a_3,\ a_3+a_1,\ a_1+a_2$	8
	$P4/mmm$	$2a_1,\ 2a_2,\ a_3$	16
	$Pm3m$	$2a_1,\ 2a_2,\ 2a_3$	32
$R\bar{3}m$	$R\bar{3}m$	$a_2+a_3,\ a_3+a_1,\ a_1+a_2$	2
	$C2/m$	$a_1+a_2,\ a_1-a_2,\ 2a_3;\ a_1$	2
	$P2/m$	$a_1+a_2,\ a_1-a_2,\ a_3$	2
	$C2/m$	$2\,(a_1+a_2),\ 2\,(a_1-a_2),\ a_3;\ 2a_1$	4
	$R\bar{3}m$	$a_2+a_3-a_1,\ a_3+a_1-a_2,\ a_1+a_2-a_3$	4
	$R\bar{3}m$	$2a_1,\ 2a_2,\ 2a_3$	8
$P6/mmm$	$P6/mmm$	$a_1,\ a_2,\ 2a_3$	2
	$Pmmm$	$a_1+a_2,\ a_1-a_2,\ a_3$	2
	$Cmmm$	$a_1+a_2,\ a_1-a_2,\ 2a_3;\ a_1+a_3$	2
	$P6/mmm$	$a_1+2a_2,\ a_1-a_2,\ a_3$	3
	$P6/mmm$	$2a_1,\ 2a_2,\ a_3$	4
	$Fmmm$	$2\,(a_1+a_2),\ 2\,(a_1-a_2),\ 2a_3;\ 2a_1,$ $a_1+a_2+a_3,\ a_1-a_2+a_3$	4
	$C2/m$	$2a_1,\ 2a_3,\ 2a_2;\ a_1+a_3$	4
	$P6/mmm$	$a_1+2a_2,\ a_1-a_2,\ 2a_3$	6
	$P6/mmm$	$2a_1,\ 2a_2,\ 2a_3$	8

and its index $[T : T_{\{k\}}]$ with respect to the translation group T of the symmetric modification, as follows from Table 66.1, does not exceed 32 *. Let us introduce $F = G/G_\Gamma$ which is the factor-group ** of the crystal space group G while G_Γ is its invariant subgroup G_Γ. The order of F does not exceed the product of the index $[T : T_{\{k\}}]$ by the order of the crystal point group K, i.e. in any case it is not more than $32 \cdot 48 = 1536$. Representation Γ of group G also serves as the representation of group F, and a precise one at that: to different $f \in F$ there correspond different matrices in representation Γ. Since representation Γ is a real one, it is possible to choose in its carrier space L a vector basis $e_1, \ldots, e_n$ (n is the dimension of the representation Γ) so that the corresponding matrices are orthogonal. Thus the abstract group F can be realized as a certain group of

* Possible values of index $[T : T_{\{k\}}]$ are equal to the values of N_t in Table 66.1 for those cases when both the Bravais lattices are related to the same system.

** For the concept of a factor-group see, e.g. Wigner (1931).

orthogonal transformations in an n-dimensional space—a subgroup of an n-dimensional orthogonal group $O(n)$. If the space group G is symmorphous, the orders of the elements of F would necessarily be crystallographic: 1, 2, 3, 4, 6. However, the representations of non-symmorphous groups G can generate groups F with certain elements of a non-crystallographic order, e.g. 8 or 12. The dimension n of representation Γ (and of space L along with it) probably does not exceed 24 *.

The components $c_1, \ldots, c_n$ of the dissymmetry parameter will be regarded as the components of a vector in space L referred to the above-mentioned basis $e_1, \ldots, e_n$ in which the matrices of representation Γ are orthogonal. The transition parameter is thus found to be a vector in space L. The transformations contained in group F generate the star of dissymmetry vectors $\{\boldsymbol{c}\}$ by their action on the dissymmetry vector. If none of the transformations of group F leaves the vector $\boldsymbol{c}$ unmoved, then the number of vectors in the star $\{\boldsymbol{c}\}$ is equal to the order of the group F. If, however, a certain subgroup F_c of the group F leaves the vector $\boldsymbol{c}$ unmoved, then the number of vectors in the star $\{\boldsymbol{c}\}$ will be equal to the index $[F : F_c]$ of the group F_c with respect to F. Vectors composing the star $\{\boldsymbol{c}\}$ correspond to individual types of domains formed under a transition. The group F_c uniquely defines the space group of the dissymmetric modification G_D: the latter is the combination of those residue classes of space group G with respect to its invariant group G_Γ which correspond to the subgroup F_c of the factor-group $F = G/G_\Gamma$

$$G_D = \sum g_i G_\Gamma, \tag{66.11}$$

where $g_i \in G$ is any representative of that residue class of group G under the subgroup G_Γ which corresponds to the element f_i of the group F_c; summation is done over group F_c. If, in particular, the group F_c comes to unity, i.e. if not a single non-unit transformation of the group F leaves the given vector $\boldsymbol{c}$ unmoved, then the group G_D simply coincides with the kernel of homomorphism G_Γ. Evidently, the index $[G : G_D]$ of the group G_D with respect to the Group G, i.e. the total reduction of symmetry under a transition is

$$N = [G : G_D] = [F : F_c]. \tag{66.12}$$

The reduction of the rotation symmetry $N_r = N/N_t$.

Thus, the problem of enumerating all space groups G_D of the dissymmetric modifications, which can be connected with the specified symmetric modification by a phase transition of the second kind, came, first, to the revealing of all irreducible representations Γ of the space group G of the symmetric modification, satisfying the milder Lifshits condition and, second, to finding for each factor-group $F = G/G_\Gamma$ all subgroups which could serve as groups F_c. The first problem is easily solved with the aid of the tables of irreducible representations of space groups (Kovalev, 1961; Faddeyev, 1961). The second problem consists in finding such subgroups of group F which would leave at least one vector unmoved; these subgroups are the n-dimensional analogues of the pyroelectric classes**. All the matrices contained in such subgroups have at least one eigenvalue equal to unity. On the other hand, the ensemble of matrices composing such a subgroup has at least one common eigenvector which corresponds to the eigenvalue equal to unity.

---

* The dimension of irreducible representations satisfying the milder Lifshits condition does not exceed 12, but some of them may be found to be complex.

** Thus this problem is the generalization for an n-dimensional case of a similar problem which was solved in a three-dimensional case by Zheludev and Shuvalov (1956) while listing all imaginable ferroelectric transitions.

The next stage of the investigation should consist in the elimination of all "excess" transitions. Along with the transitions to which there correspond representations that do not satisfy conditions (66.5), (66.8) or (66.10), there are such which can be obtained only when account is taken of the subsequent terms of expansion (66.6). To eliminate such transitions (which include, in particular, those corresponding to groups F_c that are subgroups of other such groups) it might be verified whether the given group G_D can be obtained in the course of an ordinary solution procedure which includes the substitution of expansion (66.6) in equations (66.2), the solution of these equations and the determination of space groups G_D in respect of which (66.4) will be invariant upon the substitution in it of the solutions obtained.

On the other hand, along with the transitions of the second kind, ones of the first kind close to them are also interesting. They are theoretically investigated by the methods used in the theory of the transitions of the second kind, only somewhat modified (see, e.g. the investigation of ferroelectric transitions of the first kind by Ginsburg (1949)). Of course it is not possible to draw a distinct boundary between such transitions; rather, the very possibility of specifying the symmetry and properties of a crystal near the transition temperature by means of some modification of the theory of the transition of the second kind, points to the closeness of the given transition to transitions of the second kind. From this standpoint, the list of groups G_D obtained with the aid of (66.11) can be regarded as a list containing transitions of the first kind. Let us note that much less assertive for transitions of the first kind are considerations by means of which it is proved that the dissymmetry parameter $\boldsymbol{c}$ for the transition of the second kind is transformed according to a physically irreducible representation. Since the reduction to zero of the two coefficients $A^{(m)}$ within a narrow range of temperatures is highly improbable, but not absolutely impossible, it can be expected that many, though not all, transitions of the first kind are determined by physically irreducible representations *. For the space group $Pm3m$ (O_h^1) the list of transitions of the second kind (Alexandrov, Zinenko, Mikhelson, Sirotin, 1969) can be compared with the list which also contains the transitions of the first kind defined by physically irreducible representations (Vinberg, Gufan, Sakhnenko, Sirotin, 1974).

Such is the geometric method of listing space groups G_D of dissymmetric modifications connected with the symmetric (G) modification by a phase transition of the second kind or a transition of the first kind close to the former (Sirotin, 1967; Sirotin and Mikhelson, 1969; Gufan, 1971; Vinberg, Gufan, Sakhnenko, Sirotin, 1974). The examination of groups F and F_c acting in an abstract space of representation Γ and seemingly devoid of any physical sense, is warranted by the fact that each such group combines a multitude of transitions, while the belonging of transitions to one group determines their numerous common properties that elude attention at a superficial glance. Exactly such are the transitions to the subgroup of index 2 described in Sec. 65: even though they are highly varied in their manifestations a considerable part of theoretical investigations can be carried out in a general form, thus revealing the common features of all such transitions. Transitions characterized by other groups F and F_c can be investigated in principle in a similar way. So far this method was used for the investigation of individual transitions (Sirotin, 1967; Sirotin and Mikhelson, 1969; Gufan and Sakhnenko, 1972), of the changes of physical properties, for the analysis of the domainial structure developing in transitions, etc**. Besides, there was revealed a series of common

* The transition $Pm3m$-$Pnma$ (Cochran, Zia, 1968), observed in a number of crystals (for instance, in $CaTiO_3$) can possibly be counted among the transitions defined by reducible representations.

** See also similar investigations conducted by the usual methods (Levanyuk and Sannikov, 1970; Dvořak, 1971; Dvořak, Petzelt, 1971).

properties of transitions connected with the two and three-dimensional representations, and all possible groups F and F_c for such representations were listed (Gufan and Sakhnenko, 1972a).

Alterations of the physical properties of crystals in a transition are qualitatively determined by the point groups of the symmetric and dissymmetric phases. Thus a transition turns out to be ferroelectrical, i.e. connected with the development of spontaneous polarization if and only if the numbers of the independent vector components are different for the point groups of the symmetric and dissymmetric phases (see also Zheludev and Shuvalov, 1956). Similarly, it is necessary and sufficient for these point groups that the numbers of the independent components of a symmetric second-rank tensor are different, so that spontaneous deformation can develop in the transition. These results can be made essentially more accurate if account is taken of the place occupied by the representation Γ in the system of representations of point group K. Spontaneous polarization develops in a transition both in case when the vector representation V of group K contains the representation Γ itself, and when V contains only a certain symmetric power $[\Gamma^p]$ of this representation. In the first case, however, the temperature dependence of the spontaneous polarization and dielectric permittivity is defined by (65.30) and (65.31). In the second case the spontaneous polarization increases as $|\Theta|^{p/2}$ with the increasing distance from the transition point, while the dielectric permittivity at $\Theta \to 0$ does not tend to infinity; such transitions are called singular, their feasibility was first pointed out by Indenbohm (1960a), for more details see Levanyuk and Sannikov (1974). Similarly, transitions accompanied by the development of spontaneous deformation are divided into proper ones, when representation $[V^2]$ of group K contains the representation Γ itself, and the singular ones when $[V^2]$ contains only its symmetric powers. If the translation symmetry of a crystal changes in transition, then the latter is singular with respect to all physical properties, since only the symmetric powers of representation Γ, but not Γ itself, can be contained in any representations of the point group K whatever.

The group-theoretic analysis also allows finding whether a given transition is accompanied by displacements of the equilibrium positions of atoms or not; in the former case representation Γ is contained in the vibratory representation of space group G, in the latter case it is not contained in it. This property of the transition depends in essence on the structural type of the crystal, since this type is what determines the composition of the vibratory representation of the given space group. In particular, in the structures containing atoms of a general position, any transition must be accompanied by displacements of atoms. On the contrary, in one-atomic structures the transition is accompanied by displacements of atoms only when the representation of point group $H(\boldsymbol{k})$ generated by a small representation $\Gamma_{\boldsymbol{k}}$ is contained in the vector representation of group $H(\boldsymbol{k})$. All ferroelectrical transitions are connected with displacements of atoms. Among transitions which cannot be accompanied by displacements of atoms, there are, for example, phase transitions in sodium nitrate and CuZn alloy, see Figs. 64.2 and Table 64.1. For more details see Sirotin and Mikhelson (1968); Mikhelson and Sirotin (1969).

For more information on the problems mentioned in this chapter see Barfoot (1970); Braut (1967); Vaks (1973); Zheludev (1968, 1969, 1973, 1976); Jona, Shirane (1962); Landau and Lifshits (1957, 1976); Mason (1950); Smagin and Yaroslavsky (1970); Smolensky, Bokov, Isupov et al. (1971); Smolensky and Krainik (1968); Sonin and Strukov (1970); Khachaturyan (1974).

Chapter VIII

MAGNETIC SYMMETRY IN CRYSTAL PHYSICS

Sec. 67. Time Reversal and Antisymmetry

The studies of the magnetic symmetry of crystals began, in all probability, in 1951, when the next in turn volume on theoretical physics *Statistical Physics*, by L. D. Landau and E. M. Lifshits and *Symmetry and Antisymmetry of Finite Figures* by A. V. Shubnikov were published. It was noted in *Statistical Physics* that the investigation of the symmetry of magnetic crystals must involve the operation of time reversal and its combination with translations and direct, mirror and screw rotations. Landau and Lifshits pointed out that this will lead to the occurrence of a very large number of new groups, which had not yet been derived by anybody, namely, space groups of the magnetic symmetry of crystals. Let us consider in this aspect the operation of time reversal.

Crystal physics is founded on the laws of classical mechanics and electrodynamics. These laws are invariant with respect to the group of rotations; the rotation of the reference frame to which they are referred does not change the form of these laws. They are also invariant with respect to the orthogonal group, i.e. to the totality of all possible proper and improper rotations; it must only be borne in mind that under improper rotations the vectors of the electric and magnetic fields are transformed in different ways: the former transform as ordinary (polar) vectors, and the latter as axial vectors (pseudovectors).

Moreover, if the signs of the components of the magnetic vector are reversed: $H'_i = -H_i$, the laws of mechanics and electrodynamics would be also invariant with respect to the transformation $t' = -t$, i.e. to *time reversal*. This transformation law naturally follows from the physical picture of the phenomenon: with time reversal the direction of all currents is also reversed and, consequently, the directions of all magnetic fields are also reversed as the magnetic fields are known to be generated only by currents.

Transformation $t' = -t$ is also called *time inversion*. We shall denote it by $1'$; the group consisting of a unit element and time inversion will be denoted by $1'$. Of course time inversion cannot be physically realized, just as the ordinary inversion. It is not only that we cannot make time flow backwards; we cannot transform a quartz crystal into its enantiomorph: it would have been necessary to take

the crystal apart into its individual atoms and then put the atoms together again in a different order*. The definition of symmetry transformation simply must not include the assumption of the physical feasibility of this transformation.

If to the orthogonal group $\infty\infty\bar{1}$** the operation of time inversion $1'$ and all its possible combinations with proper and inversion rotations are joined an *expanded orthogonal group* $\infty\infty\bar{1}1'$ will result. The basic physical laws are invariant with respect to this group. They are also invariant with respect to the translations. On the whole all possible combinations of translations with operations of the expanded orthogonal group define an *expanded Euclidean group.*

All transformations of crystal symmetry together constitute the crystal symmetry group. If it consists only of the transformations that leave physical laws invariant, it can be naturally called the *group of physical symmetry* of crystals. This relates to all point and space crystallographic groups and all crystallographic subgroups of the expanded orthogonal and expanded Euclidean groups.

Now let us turn to ideas of antisymmetry. The first of them is the generalized concept of equality: along with equal figures we consider *antiequal* ones. The simplest example of antiequal figures is that of two geometrically equal but differently coloured figures: a black figure is antiequal to an equal white one, and the white figure is antiequal to the black one. Thus in Escher's picture "Day and night" (Fig. 67.1): a black (night) town is antiequal to a white (day) one, a black river is antiequal to the light one, black birds to white ones.

A. V. Shubnikov points out that any figures of the same dimensions, mutually opposite in some property can be considered antiequal: opposite in colouring, in the sign of electric charge, the direction of magnetic moment, and so on. Thus, white or black colouring of a figure is merely a conventional designation of the fact that this figure has, besides geometric properties, some property and that this property can be characterized by a quantity with two values only, say, $+1$ and -1. In the context of antisymmetry we can also consider properties characterized by a quantity which can have three values: $+1$, -1 and 0. This corresponds to the consideration, along with black and white figures, also of "grey" figures, or along with positively and negatively charged figures also of ones that have no charge, of neutral figures.

Along with symmetry operations there are introduced *antisymmetry* operations. While a symmetry operation transforms a figure into

* In a general case—to divide an enantiomorphous body into non-enantiomorphous parts and to build an enantiomorph of them again. At least in principle the presence of such non-enantiomorphous parts at some level of the division is an imperative condition of the feasibility of this operation.

** In this context it is more convenient to use notation $\infty\infty\bar{1}$ than the equivalent but more customary $\infty\infty m$.

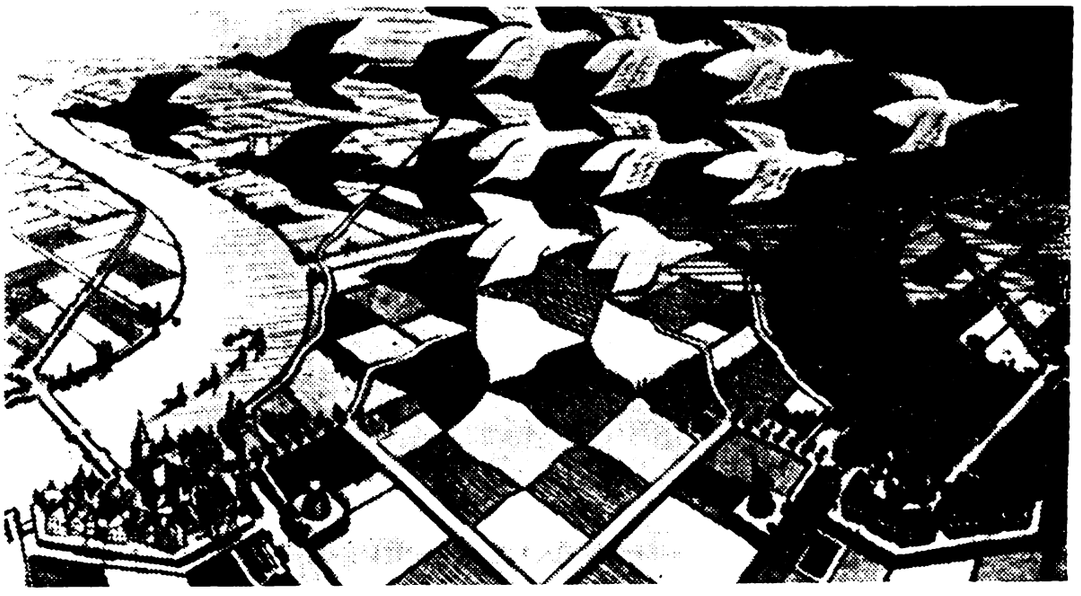


Fig. 67.1. Escher. "Day and Night".

the same one, i.e. an equal figure, an antisymmetry operation transforms it into an antiequal one. Thus an *operation of antiidentification* and all its possible combinations with orthogonal transformations are introduced into consideration.

The operation of antiidentification, I' (Shubnikov uses the symbol $\bar{I}$, but his notation differs from the international system in general, see Sec. 5), as applied to the black-white figures, consists in the change of colour: everything that was white prior to the operation became black after it, everything that was black became white. If the figures are imagined to be colourless but electrically charged, the action of antiidentification will result in the reversal of the charge sign.

Apparently, none of the white or black figures can be invariant with respect to the operation of antiidentification. Therefore along with black and white figures there are introduced into consideration grey figures, which by definition upon antiidentification transform into themselves. If an "electric" interpretation of antisymmetry is adopted, i.e. if it is considered that antiidentification transforms a body into the same body of an opposite charge, it will be clear that invariance with respect to antiidentification is the property of all unchanged, electrically neutral bodies.

Combinations of antiidentification with simple and mirror rotations are called *antirotations* and denoted by symbols of the corresponding rotations with an oblique prime (according to Shubnikov, with a minus sign under the rotation symbol). Antirotation is a transformation consisting of a rotation and a change of colour; the sequence in which these operations are performed is of no importance.

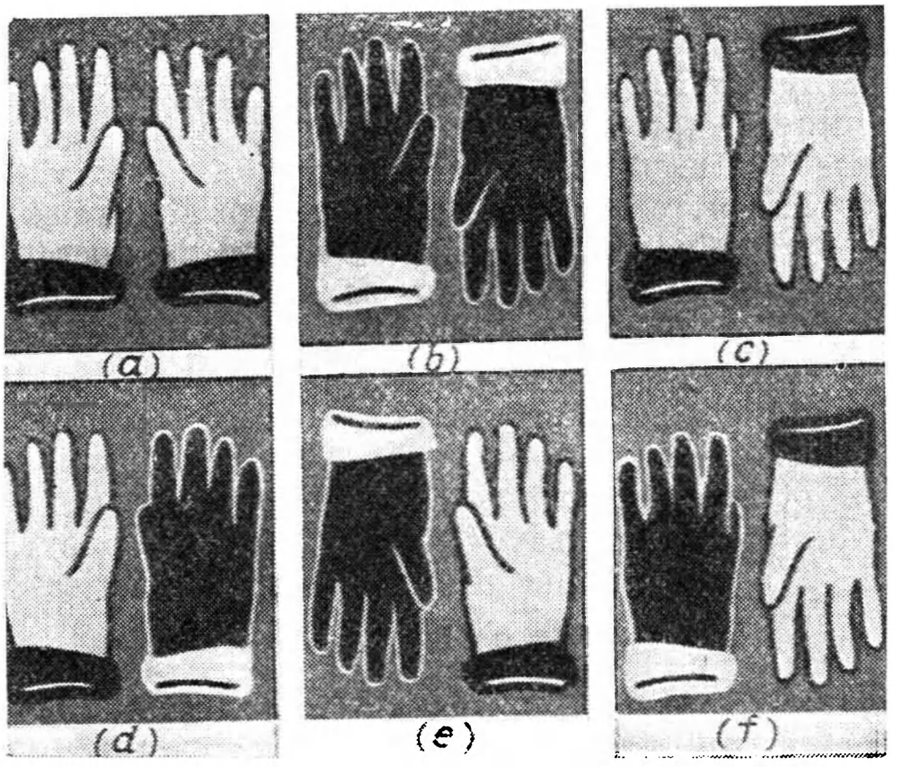


Fig. 67.2. Simplest symmetric (a, b, c) and antisymmetric (d, e, f) figures, according to A. V. Shubnikov. The symmetry of figures: (a) symmetry plane m, (b) symmetry axis 2, (c) centre of symmetry $\bar{1}$, (d) antisymmetry plane m', (e) antisymmetry axis $2'$, (f) centre of antisymmetry $\bar{1}'$

Point groups of antisymmetry (in the broad sense of the word) consist of a group containing all possible simple and mirror rotations and antirotations and all its subgroups. Among the latter are ordinary symmetry groups G; they include only ordinary, both simple and mirror, rotations. These groups are represented as figures of one colour, or, as Shubnikov calls them, *polar* figures (they are usually shown in white, but could be just as well shown in black). Groups containing the antiidentification operation performed by itself are denoted by $G1'$, and represented just like G but by grey figures; Shubnikov calls such figures *neutral*. Finally, essentially new groups, i.e. groups G' containing some of the antirotations, but no antiidentification, are represented by figures with both black and white parts, i.e. by figures of *mixed polarity*. These names are transferred to the groups too; G are polar, or white groups; $G^{1\prime}$ are neutral, or grey groups; G' are groups of mixed polarity, or black-white groups. We wish to note that often antisymmetry groups are restricted only to groups of mixed polarity. Figures characterizing some of such groups are shown in Fig. 67.2.

When Tavger and Zaitsev (1956), proceeding from some ideas contained in *Statistical Physics*, derived point groups of the magnetic symmetry of crystals, the groups were found to be isomorphous to

antisymmetry point groups described in Shubnikov's book. Thus groups of magnetic symmetry of crystals differ from antisymmetry groups only by their interpretation. More precisely, among many imaginable interpretations of antisymmetry point groups there is possible their interpretation as of magnetic symmetry groups, but it is just this interpretation that leads to groups of physical symmetry of crystals. With this in mind we have denoted the operation of anti-identification by the same symbol $1'$ as is used for time reversal.

After Shubnikov had suggested the possibility and, moreover, the necessity of the generalization of the classical teaching of symmetry, and had made some progress in this direction himself, having constructed antisymmetry point groups, his investigations attracted the attention of many scientists. Soon the space groups of antisymmetry were derived (Zamorzayev, 1957; Belov, Neronova and Smirnova, 1955, 1957) and further generalization of classical symmetry, namely, colour symmetry was suggested (Belov and Tarkhova, 1956; Indenbohm, Belov and Neronova, 1960; Zamorzayev, 1967, 1970). Various generalization of the classical theory of symmetry can be classified and derived from common positions with the aid of methods of the group expansion theory (Shubnikov and Koptsik, 1972).

Sec. 68. Point Groups of Magnetic Symmetry

The expanded orthogonal group and all its subgroups are called the point groups of magnetic symmetry. The expanded orthogonal group consists of all possible orthogonal transformations g, as well as of the same transformations multiplied by time inversion; we shall denote them by g'. Because of the commutation of time inversion with all orthogonal transformations, and of the inversion square being an identical transformation, the following multiplication rules result:

if

$$g_i g_j = g_k, \quad g_j g_i = g_l,$$

then

$$\begin{aligned} g'_i g_j &= g'_k, & g_j g'_i &= g'_l, \\ g_i g'_j &= g'_k, & g'_j g_i &= g'_l, \\ g'_i g'_j &= g_k, & g'_j g'_i &= g_l. \end{aligned} \tag{68.1}$$

Let us discuss crystallographic groups (i.e. groups containing rotations and antirotations only through angles $\pi/2$, $\pi/3$, and their multiples) and limit groups of magnetic symmetry. They are sometimes also called the *classes of magnetic symmetry*.

Of course, to begin with, they contain 32 ordinary crystallographic groups and 7 ordinary limit groups. These groups can be regarded as

groups of magnetic symmetry containing no antirotations, time inversion included. These are white, or polar, groups G.

Next, the point groups of magnetic symmetry contain 39 grey (neutral) groups $G1'$: these are 32 crystallographic and 7 limit groups. Each of them contains time inversion, and any rotation g is included in the group together with the corresponding antirotation g'.

Finally, the third type of magnetic symmetry groups is formed by black-white groups, or groups of mixed polarity G'. Time inversion is not included in either of them, but along with proper or inversion rotations $h_1, \ldots, h_k$ there are always included antirotations $g'_1, \ldots, g'_l$. Since $1'$ is not included in the group, none of the g_j operations coincides with any of the operations h_i. Rotations h_i form group H which is a crystallographic (i.e. non-magnetic) subgroup of group G', while antirotations form a set $G' - H$.

Having fixed a certain antirotation g'_j let us consider all possible products $g'_j h_i$, where h_i passes through the whole group H. They are all different and by virtue of (68.1) belong to the set $G' - H$. Therefore the number of elements in the set is not less than in group H. On the other hand, having examined all possible products $g'_j g'_i$ at a fixed g'_j and element g'_i passing through the whole set $G' - H$ we find that they also are all different and by virtue of (68.1) belong to group H, so that the number of elements in it is no less than in $G' - H$. It is evident that these numbers are simply equal to each other and that H is a subgroup of group G' of index 2.

Upon cancelling the primes in elements g' it is possible to obtain the crystallographic group $G = \{h_1, \ldots, h_k, g_1, \ldots, g_k\}$ from any black-white group G'. And conversely, the black-white group G' can be obtained from any crystallographic group G containing subgroup H of index 2 by multiplying elements g_j not included in subgroup H, by time inversion. The totality of rotations h_i and antirotations g'_j constitutes the sought-for black-white group G', and all such groups can be obtained by this method.

Let us find out, for instance, what black-white groups can be obtained from group $\bar{4}2m$. This is an eight-order group. It has three subgroups of index 2, namely, 4, 222 and $mm2$. Let us examine them consecutively. Of the group $\bar{4}2m$ elements

included in the subgroup $\bar{4}$ are	$1, 2_z, \bar{4}_z, \bar{4}^3_z$,
not included in it are	$2_x, 2_y, m_u, m_v$;
included in the subgroup 222 are	$1, 2_z, 2_x, 2_y$;
not included in it are	$\bar{4}_z, \bar{4}^3_z, m_u, m_v$;
included in the subgroup $mm2$ are	$1, 2_z, m_u, m_v$;
not included in it are	$2_x, 2_y, \bar{4}_z, \bar{4}^3_z$.

Having substituted orthogonal transformations not belonging to

subgroup H by corresponding antirotations we arrive at the following black-white groups:

$$\{1, 2_z, \bar{4}_z, \bar{4}_z^3, 2'_x, 2'_y, m'_u, m'_v\} = \bar{4}2'm';$$

$$\{1, 2_z, 2_x, 2_y, \bar{4}'_z, \bar{4}_z^{3\prime}, m'_u, m'_v\} = \bar{4}'2m';$$

$$\{1, 2_z, m_u, m_v, 2'_x, 2'_y, \bar{4}'_z, \bar{4}_z^{3\prime}\} = \bar{4}'2'm;$$

they are shown in Fig. 68.1.

Other crystallographic black-white groups are easily obtained by the same method (see, e.g. Fig. 68.2).

All crystallographic and limit* groups G, their subgroups H of index 2 and the corresponding black-white groups G' are given in

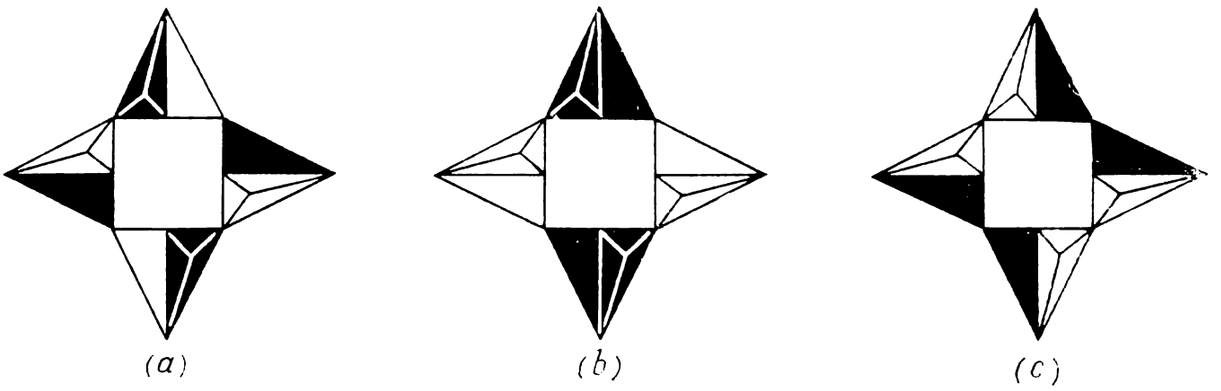


Fig. 68.1. Figures of black and white tetrahedrons belonging to antisymmetry point groups, connected with the crystallographic group $G = \bar{4}2m$: (a) $G' = \bar{4}2'm'$, (b) $G' = \bar{4}'2m'$, (c) $G' = \bar{4}'2'm$

Table 68.1. Calculation shows that there are 58 crystallographic black-white groups and 7 limit groups. All in all there are 143 magnetic symmetry point groups of different types: 122 crystallographic and 21 limit groups.

International notation of crystallographic groups of magnetic symmetry is defined by the following conventions:

(1) the polar (white) group G is denoted just as a crystallographic group consisting of the same transformations;

(2) the neutral (grey) group $G1'$ is denoted by a symbol of the corresponding crystallographic group G with the addition of $1'$ for example, $321'$, $m3m1'$; the neutral character of the group can also be indicated by the sign $3'$ in the symbol; so, instead of $321'$ and $m3m1'$ we can write $3'2$ and $m3'm$ respectively;

(3) notation for the group of mixed polarity G' (black-white group) differs from the international one of a corresponding crystallograph-

* The simplest determination of black-white limit groups is based on the following theorem: if point group G has a sign-alternating representation (i.e. a representation consisting of numbers 1 and —1), then a black-white group G' can be constructed by leaving unchanged those elements of the group G to which there corresponds 1 in the given representation, and multiplying other elements by time inversion (Indenbohm, 1959).

ic group G only by the addition of a prime which signifies an anti-operation in the symbol, for example, $m'3m$ means that a reflection in planes {100} is accompanied by time inversion, $m3m'$ means the same for planes {110}, while $m'3m'$ means the same for both planes*.

Crystallographic groups of magnetic symmetry are used for the description of crystal symmetry accounting for the magnetic ordering of their structure; limit groups can be used, in particular, to characterize the symmetry of quantities contained in Maxwell's system of equations.

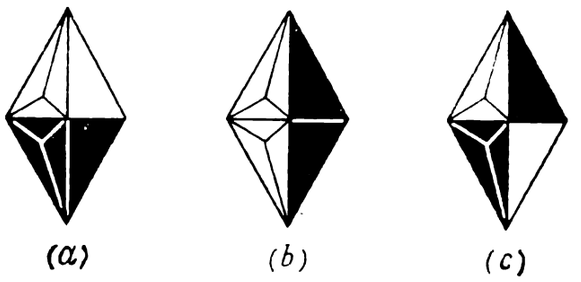


Fig. 68.2. Figures of black and white tetrahedrons belonging to antisymmetry point groups, connected with the crystallographic group $G = 2/m$: (a) $G' = 2/m'$, (b) $g' = 2'm$, (c) $G' = 2'/m'$

Electric Charge e. This is a scalar which does not reverse its sign under time inversion. Thus it is invariant with respect to all transformations of the expanded orthogonal group $\infty\infty\bar{1}, 1'$, which should therefore be considered its symmetry group. The same is of course the symmetry of the mass of particle m.

Electric Field Strength $\boldsymbol{E}$. This is a polar vector which does not reverse its direction under time inversion. Its group of magnetic symmetry includes the symmetry group of the polar vector $\infty\, m$ and the group $1'$—this is the limit group $\infty m1'$. The radius-vector $\boldsymbol{r}$ has the same symmetry as vector $\boldsymbol{E}$.

Magnetic Field Intensity $\boldsymbol{H}$. This is an axial vector which reverses its direction with time inversion. The reflection in a plane parallel to the principal axis also reverses the direction of the axial vector. It is evident that the combination of such a reflection with time inversion does not reverse the direction of vector $\boldsymbol{H}$ and, consequently, is a symmetry element for it. Therefore the symmetry group of the vector of the magnetic field intensity contains, as subgroups, the symmetry group of axial vector ∞/m and group m' (plane m' being parallel to the axis ∞). This is the limit group ∞/mm'.

Let us determine, for exercise, the symmetry of a *magnetic charge*, if such charges could exist at all. It would be a pseudoscalar reversing its sign with time inversion. It is apparent that such a quantity must be invariant with respect to space-time inversion (antiinversion). Its symmetry is therefore $\infty\infty\,\bar{1}'$.

* Along with the international notation of magnetic symmetry point groups Shubnikov's notation (see Sec. 5 and Table 6.1) is also used. The latter is obtained from Shubnikov's notation of crystallographic groups in accordance with almost the same conventions. The only difference is that the prime is replaced by a minus sign under the corresponding symbol, e.g. groups $\bar{4}2'm'$, $\bar{4}'2m'$ and $\bar{4}'2'm$ are denoted according to Shubnikov as $\bar{4} : 2$, $\bar{4} : 2$, and $\bar{4} : \bar{2}$ respectively.

Table 68.1

Black-White Crystallographic and Limit Groups of Magnetic Symmetry

G	H	G'	G	H	G'	G	H	G'
1	—	—	$4/m$	$\bar{4}$	$4'/m'$	$-m2$	$3m$	$\bar{6}'m2'$
$\bar{1}$	1	$\bar{1}'$	422	222	$4'22'$	$\bar{6}m2$	$\bar{6}$	$\bar{6}m'2'$
2	1	$2'$	422	4	$42'2'$	$6/mmm$	$\bar{3}m$	$6'/m'mm'$
m	1	m'	$4mm$	$mm2$	$4'mm'$	$6/mmm$	$6/m$	$6/mm'm'$
$2/m$	$\bar{1}$	$2'/m'$	$4mm$	4	$4m'm'$	$6/mmm$	622	$6/m'm'm'$
$2/m$	2	$2/m'$	$\bar{4}2m$	222	$\bar{4}'2m'$	$6/mmm$	$6mm$	$6/m'mm$
$2/m$	m	$2'/m$	$\bar{4}2m$	$mm2$	$\bar{4}'2'm$	$6/mmm$	$\bar{6}m2$	$6'/mmm'$
222	2	$22'2'$	$\bar{4}2m$	$\bar{4}$	$\bar{4}2'm'$	23	—	—
$mm2$	2	$m'm'2$	$4/mmm$	mmm	$4'/mmm'$	$m3$	23	$m'3$
$mm2$	m	$mm'2'$	$4/mmm$	$4/m$	$4/mm'm'$	432	23	$4'32'$
mmm	$2/m$	$mm'm'$	$4/mmm$	422	$4/m'm'm'$	$\bar{4}3m$	23	$4'3m'$
mmm	222	$m'm'm'$	$4/mmm$	$4mm$	$4/m'mm$	$m3m$	$m3$	$m3m'$
mmm	$mm2$	mmm'	$4/mmm$	$\bar{4}2m$	$4'/m'm'm$	$m3m$	432	$m'3m'$
3	—	—	6	3	$6'$	$m3m$	$\bar{4}3m$	$m'3m$
$\bar{3}$	3	$\bar{3}'$	$\bar{6}$	3	$\bar{6}'$	∞	—	—
32	3	$32'$	$6/m$	$\bar{3}$	$6'/m'$	∞/m	∞	∞/m'
$3m$	3	$3m'$	$6/m$	6	$6/m'$	$\infty 2$	∞	$\infty 2'$
$\bar{3}m$	$\bar{3}$	$\bar{3}m'$	$6/m$	$\bar{6}$	$6'/m$	∞m	∞	$\infty m'$
$\bar{3}m$	32	$\bar{3}'m'$	622	32	$6'22'$	∞/mm	∞/m	∞/mm'
$\bar{3}m$	$3m$	$\bar{3}'m$	622	6	$62'2'$	∞/mm	$\infty 2$	$\infty/m'm'$
4	2	$4'$	$6mm$	$3m$	$6'mm'$	∞/mm	∞m	$\infty/m'm$
$\bar{4}$	2	$\bar{4}'$	$6mm$	6	$6m'm'$	$\infty\infty$	—	—
$4/m$	$2/m$	$4'/m$	$\bar{6}m2$	32	$\bar{6}'m'2$	$\infty\infty m$	$\infty\infty$	$\infty\infty m'$
$4/m$	4	$4/m'$						

The point groups of the crystal magnetic symmetry interpreted as antisymmetry groups can be used for specifying the symmetry (more precisely, the antisymmetry) of odd-type matter tensors (see Sec. 44). Their use is based on the following arguments. The action of inversion on odd-type tensors consists in the multiplication of all their components by —1, this operation being naturally regarded as an antiidentification: $\bar{1} \to 1'$. This operaton in itself is certainly absent from the antisymmetry groups of the odd-type tensors, but its multiplication by the operatons included in the symmetry group of the tensor leads to the tensor's antisymmetry.

Let, for example, a symmetry plane m be among the symmetry elements of an odd-type tensor. Since $m = 2\cdot\bar{1}$, and $\bar{1} \to 1'$ then $m \to 2\cdot 1' = 2'$, i.e. it follows from the availability of a symmetry plane in the odd-type tensor that it also has a 2-fold antisymmetry axis perpendicular to the plane. This means that under rotation of the tensor (or the coordinate frame) by 180° about the direction

perpendicular to the symmetry plane all its components will reverse their signs. And indeed, in Fig. 44.2 one of the stereographic projections of the representation surface of the longitudinal piezoelectric effect in a tourmaline crystal (class $3m$) is constructed so that the plane of projection X_2X_3 coincides with one of the crystal's symmetry planes. Axis X_1 perpendicular to it must therefore serve as a 2-fold antiaxis: $2' \parallel X_1$, which it actually is, as can be clearly seen in the projection.

Another example: let an odd-type tensor have a 2-fold symmerty axis. Since $2 = m \cdot \bar{1}$, then $2 \rightarrow m'$, i.e. it follows from the availability of a 2-fold axis in the odd-type tensor that it also has a plane of antisymmetry perpendicular to the axis. This can be seen in Figs. 58.2 and 58.3 which are stereographic projections of the representation surfaces of the longitudinal piezoelectric effect in crystals of ethylene diaminetartrate and lithium sulphate (class 2). Axis $2 \parallel X_2$ is not visible in the stereograms (it is possible therefore to give only the front circle of projection), while the antisymmetry plane $m' \perp X_2$ perpendicular to it can be seen quite distinctly.

Insofar as an antisymmetry group contains, together with a symmetry plane, a 2-fold antiaxis perpendicular to the plane, and together with the 2-fold axis, an antiplane perpendicular to it, the antisymmetry group must also contain the product of these elements—an anticentre of symmetry (or a centre of antisymmetry) $\bar{1}'$. It is contained in the antisymmetry group of any odd-type tensor: indeed if the tensor is multiplied by -1 both under inversion $\bar{1}$ and under antiidentification $1'$, then it is invariant with respect to the product of these operations $\bar{1}'$. Thus, while even-type tensors are centrosymmetric, odd-type tensors are anticentrosymmetric.

Table 68.2

Antisymmetry Groups of Odd-Type Tensors
(G is a Symmetry Group, G' is an Antisymmetry Group)

G	G'	G	G'	G	G'
1	$\bar{1}'$	$\bar{4}$	$4'/m'$	23	$m'3$
2	$2/m'$	422	$4/m'm'm'$	432	$m'3m'$
m	$2'/m$	$4mm$	$4/m'mm$	$\bar{4}3m$	$m'3m$
222	$m'm'm'$	$\bar{4}2m$	$4'/m'mm'$	∞	∞/m'
$mm2$	mmm'	6	$6/m'$	$\infty\, 2$	$\infty/m'm'$
3	$\bar{3}'$	$\bar{6}$	$6'/m$	$\infty\, m$	$\infty/m'm$
32	$\bar{3}'m'$	622	$6/m'm'm'$	$\infty\, \infty$	$\infty\, \infty\, m'$
$3m$	$\bar{3}'m$	$6mm$	$6/m'mm$		
4	$4/m'$	$\bar{6}m2$	$6'/mmm'$		

This fact facilitates finding antisymmetry groups G' (T) of odd-type tensors T: for constructing the group G' (T) it will suffice to add the antisymmetry centre $\bar{1}'$ and its products by all the $g \in G$ (T) to the symmetry group G (T). Obviously all groups G' (T) thus obtained will be black-white.

The limit antisymmetry groups are constructed similarly. So the symmetry group of a vector G $(V) = \infty\, m$; its antisymmetry group G' $(V) = \infty/m'm$ is clearly seen in Fig. 22.3 which shows the vector's representation surface. The symmetry group of a third-rank tensor **e** (see Sec. 42), antisymmetric with respect to all indices, is G (**e**) $= \infty\infty$, its antisymmetry group is G' (**e**) $= \infty\infty m'$.

Table 68.2 shows the antisymmetry group G' of any odd-type tensor possessing symmetry group G.

Sec. 69. Space Groups of Magnetic Symmetry—Shubnikov's Groups

Space groups of magnetic symmetry were named *Shubnikov's groups* in honour of academician A. V. Shubnikov, the founder of the teaching on antisymmetry; they are discrete subgroups of the expanded Euclidean group. Thus Shubnikov's groups are a natural generalization of Fedorov's groups which represent the discrete subgroups of the ordinary Euclidean group.

Shubnikov's groups include, first, the same transformations as those contained in ordinary space groups: translations, ordinary inversion and screw rotations through angles $\pi/2$, $\pi/3$ and their multiples, mirror and glide reflections and inversions, and, second, the same transformations accompanied by time inversion: antitranslations, ordinary, inversion and screw antirotations, mirror and glide antireflections, and antiinversions.

Just as to every space group there corresponds one, and only one, point group defining the class of crystals that have the given space group, so to every Shubnikov's group there corresponds one, and only one, crystallographic point group of magnetic symmetry which defines the magnetic symmetry class of all crystals having the given Shubnikov group. When among transformations contained in a Shubnikov group all translations are replaced by identifications and all antitranslations are replaced by antiidentifications, we shall obtain the point group of magnetic symmetry corresponding to the given Shubnikov group.

Generally speaking, several Shubnikov's groups correspond to each class of magnetic symmetry: there are a little over a hundred classes of magnetic symmetry, while the number of Shubnikov's groups exceeds fifteen hundred.

To begin with, the Shubnikov groups contain 230 ordinary space (Fedorov's) groups. When regarded as Shubnikov's groups, they are found to contain no antioperations, i.e. they are *white*, or *polar*, *groups*; we shall denote them by symbol Φ. Since there are no antioperations in the composition of these groups, there can be none in the composition of magnetic symmetry point groups corresponding to these Shubnikov's groups. Thus, to the 230 white, or polar, Shubnikov's groups Φ there correspond 32 point groups G which are white too.

Next, Shubnikov's groups have 230 groups containing, along with every operation, a corresponding antioperation: along with translations—the same antitranslations, along with rotations—antirotations of the same kind and through the same angles, and so on; we shall call them *grey*, or *neutral*, groups and denote them by $\Phi 1'$. To each of the neutral Shubnikov groups there obviously corresponds some point group, also neutral, of magnetic symmetry, and to all 230 neutral Shubnikov's groups $\Phi 1'$ there correspond 32 neutral point groups $G1'$ of magnetic symmetry.

Finally, besides the above 460 Shubnikov groups, obtained actually without derivation, there are also Shubnikov's groups Φ' of *mixed polarity*, or *black-white* groups. Time inversion by itself is not included in either of them, but some antioperations are always contained in every group. These groups were derived by Zamorzaev (1957, 1967), and, quite independently, by Belov, Neronova and Smirnova (1955, 1957). There were found 1191 such groups.

In groups of this type operations never correspond to antioperations: if a group Φ' contains a rotation through a certain angle or a translation by a certain vector, it is not able to contain either an antirotation through the same angle, or an antitranslation by the same vector. Ordinary operations form a Fedorov subgroup F with index 2 of the given Shubnikov group Φ'. If all antioperations of group Φ' are replaced by corresponding ordinary operations we shall obtain a Fedorov group Φ: with respect to it F will be a subgroup with index 2. Therefore the method of derivation of black-white space groups of magnetic symmetry does not differ in principle from the derivation of black-white point groups: it requires a consecutive scanning of all subgroups of index 2 of the Fedorov groups Φ. Leaving unchanged the operations contained in subgroup F we substitute the remaining operations of group Φ by the corresponding antioperations. The resulting totality of operations and antioperations represents Shubnikov's group Φ'. This is the way to derive all Shubnikov's groups of mixed polarity.

Shubnikov's groups of mixed polarity are of two types, since the subgroups F of index 2 of the Fedorov groups Φ can be also, generally speaking, of two types. Let G be a point group corresponding to space group Φ. To space group F there can correspond either (a) point

group H, which is a subgroup of index 2 with respect to point group G, or (b) the same point group G which also corresponds to space group Φ*.

If subgroup F is related to type (a), it has only half the rotation elements of group Φ, but all the translations of the latter group are also contained in F. But if subgroup F is related to type (b), it contains the same rotation elements as in group Φ, but roughly speaking only half of the latter's translations; this means that the volume of elementary cell in group F is twice that of group Φ.

Now let us pass from the Fedorov groups Φ to black-white Shubnikov's groups Φ' corresponding to them. If the Fedorov subgroup F of a given Shubnikov group Φ' is related to type (a), then to the black-white space group Φ' there will correspond another also black-white point group G'. Indeed, if point group G corresponds to the Fedorov group Φ, and its subgroup H—to the Fedorov subgroup F, it is apparent that to the Shubnikov group Φ' there corresponds a black-white point group G' for which H is a crystallographic subgroup**.

If the Fedorov subgroup F of group Φ' relates to type (b), then to the black-white Shubnikov group Φ' there corresponds the grey point group $G1'$. In actual fact, in this case the Fedorov subgroup F of group Φ' does not contain all the translations included in the latter group, this meaning that the Shubnikov group Φ' contains antitranslations. In a transition from a space group to the corresponding point group all translations are replaced by identification, and antitranslations by antiidentification; the latter is contained only in the grey groups. Therefore, if to the Fedorov group Φ and its subgroup F of index 2 there corresponds one and the same point group G, then to the Shubnikov group Φ' there corresponds point group $G1'$. Table 69.1 gives the number of Shubnikov's groups of different types.

In practice Shubnikov's groups are denoted by a modified system of international notation for space groups suggested by N. V. Belov, N. N. Neronova and T. S. Smirnova***; the A. M. Zamorzaev system has not apparently been accepted for general use. The international notation of Shubnikov's groups is defined by conventions in no way differing from similar conventions for point groups of magnetic symmetry. The only supplement is required for denoting those black-white Shubnikov's groups to which grey point groups correspond.

---

* The same division of subgroups F of index 2 into two types can be defined in another way: subgroup F of the group Φ is related to type (a), if its translation subgroup coincides with the translation subgroup of group Φ, and to type (b) in the opposite case. See Boyle and Lawrenson (1972).

** Cf. symbol Φ/F of the Shubnikov group Φ' introduced by Koptsik (1966).

*** See their paper published in 1955; a list of all Shubnikov's groups is also contained in a monograph by V. A. Koptsik (1966).

Table 69.1

Number of Shubnikov's Groups of Different Types

Shubnikov's groups	Number of groups corresponding to point groups			Total
	to 32 white ones (G)	to 32 grey ones ($G1'$)	to 58 black-white ones (G')	
White (Φ)	230	—	—	230
Grey ($\Phi 1'$)	-	230	—	230
Black-white (Φ')	—	517	674	1191
Total	230	747	674	1651

In the notation of these groups the Bravais lattice symbol is supplied with index showing the direction of antitranslation.

A small letter in an index shows that the antitranslation is directed along a corresponding edge of the elementary cell; a capital A, B or C shows that the antitranslation is directed toward the centre of a corresponding face; a capital I shows that it is directed toward the centre of the elementary cell.

The type of a Shubnikov group and the point group of magnetic symmetry corresponding to it are easily determined from the international notation. If the notation of a Shubnikov group coincides with that of some Fedorov's group (i.e. contains neither primes, nor indices in the lattice symbol), this means that it is one of the white (polar) Shubnikov groups. If the group symbol contains $1'$ or $3'$, it is a grey (neutral) Shubnikov group. If a group symbol contains other symmetry elements with primes it means that we have to deal with one of the black-white Shubnikov groups of the black-white class of magnetic symmetry. Finally, an index at a letter showing the type of the Bravais lattice allows referring the given group to the black-white Shubnikov groups included in grey (neutral) class of magnetic symmetry.

Let us give an example of the derivation of Shubnikov's groups: let us list all the Shubnikov groups derived from the Fedorov group $P2$. There is given below the set of elements* of group $\Phi = P2$ which contains all the generating elements of its subgroups F of index 2. Then there are given the lists of generating elements of subgroups F. There is written under each such a subgroup a corresponding Shubnikov group Φ' (denoted by Koptsik symbol Φ/F).

* Strictly speaking, they should be denoted by $[h/t]$ where h is the rotation, t is the translation, but operations of the form of $[h/0]$ and $[1/t]$ are denoted for brevity by h and t respectively.

Antitranslations are denoted by vectors with primes.

$$P2 = \{1,\ 2_y,\ \boldsymbol{a}_1,\ \boldsymbol{a}_2,\ \boldsymbol{a}_3,\ 2\boldsymbol{a}_1,\ 2\boldsymbol{a}_2,\ \boldsymbol{a}_1+\boldsymbol{a}_2,\ \ldots\}$$
$$P1 = \{1,\ \ \boldsymbol{a}_1,\ \boldsymbol{a}_2,\ \boldsymbol{a}_3,\ 2\boldsymbol{a}_1,\ 2\boldsymbol{a}_2,\ \boldsymbol{a}_1+\boldsymbol{a}_2,\ \ldots\}$$
$$P2' = \{1,\ 2'_y,\ \boldsymbol{a}_1,\ \boldsymbol{a}_2,\ \boldsymbol{a}_3,\ 2\boldsymbol{a}_1,\ 2\boldsymbol{a}_2,\ \boldsymbol{a}_1-\boldsymbol{a}_2,\ \ldots\}$$
$$P2 = \{1,\ 2_y,\ \ \boldsymbol{a}_2,\ \boldsymbol{a}_3,\ 2\boldsymbol{a}_1,\ 2\boldsymbol{a}_2,\ \ldots\}$$
$$P_a2 = \{1,\ 2_y,\ \boldsymbol{a}'_1,\ \boldsymbol{a}_2,\ \boldsymbol{a}_3,\ 2\boldsymbol{a}_1,\ 2\boldsymbol{a}_2,\ \boldsymbol{a}'_1+\boldsymbol{a}'_2,\ \ldots\}$$
$$P2 = \{1,\ 2_y,\ \boldsymbol{a}_1,\ \ \boldsymbol{a}_3,\ 2\boldsymbol{a}_1,\ 2\boldsymbol{a}_2,\ \ldots\}$$
$$P_b2 = \{1,\ 2_y,\ \boldsymbol{a}_1,\ \boldsymbol{a}'_2,\ \boldsymbol{a}_3,\ 2\boldsymbol{a}_1,\ 2\boldsymbol{a}_2,\ \boldsymbol{a}'_1+\boldsymbol{a}'_2,\ \ldots\}$$
$$C2 = \{1,\ 2_y,\ \ \boldsymbol{a}_3,\ 2\boldsymbol{a}_1,\ 2\boldsymbol{a}_2,\ \boldsymbol{a}_1+\boldsymbol{a}_2,\ \ldots\}$$
$$P_C2 = \{1,\ 2_y,\ \boldsymbol{a}'_1,\ \boldsymbol{a}'_2,\ \boldsymbol{a}_3,\ 2\boldsymbol{a}_1,\ 2\boldsymbol{a}_2,\ \boldsymbol{a}_1+\boldsymbol{a}_2,\ \ldots\}$$

Group P_c^2 is absent from this list because it differs from P_a2 only in notation.

Point groups and Bravais lattices of the obtained Shubnikov groups are the following:

Shubnikov's group	$P2'$	P_a2	P_b2	P_C2
Point group	$2'$	$21'$	$21'$	$21'$
Bravais lattice	$P2/m$	P_a2/m	P_b2/m	P_C2/m

The first group is related to type (a), the other three to type (b).

Sec. 70. Magnetic Symmetry of Crystals

The electric and magnetic* structure of crystals can be described, after Landau and Lifshits (1957), with the aid of two coordinate functions: a scalar function $\rho(\boldsymbol{r})$ describing the true (microscopic) time-mean value of the electric charge density (but not the elementary volume mean value!), and a vector function $\boldsymbol{j}(\boldsymbol{r})$ describing the current density which has been averaged in a similar way. The former function defines the electric structure of a crystal, the latter,— a crystal's magnetic structure: if the charge ρ or current $\boldsymbol{j}$ densities are not identically zero, it is said that the crystal has an electric or a magnetic structure respectively. Actually, all crystals have the electric structure, while comparatively few have the magnetic structure.

The functions $\rho(\boldsymbol{r})$ and $\boldsymbol{j}(\boldsymbol{r})$ must satisfy some definite conditions. It is evident, for example, that the condition of the neutrality of each elementary cell and consequently of the crystal as a whole is

* On magnetism see Vonsovsky (1971).

satisfied*

$$\int_V \rho \, dV = 0. \tag{70.1}$$

A crystal in the state of equilibrium must also have no macroscopic current, i.e.

$$\int_V \boldsymbol{j} \, dV = 0. \tag{70.2}$$

The magnetic moment per unit volume

$$\boldsymbol{m} = \frac{1}{V} \int_V \boldsymbol{r} \times \boldsymbol{j} \, dV \tag{70.3}$$

can differ from zero, however, and the crystal is then called a *ferromagnetic*. If the density of the microscopic current $\boldsymbol{j}$ is not identically zero, but $\boldsymbol{m} = 0$, then the crystal is an *antiferromagnetic*. In the latter case elementary cells can be divided into parts whose magnetic moments differ from zero, and only their sum is zero.

Group G of the microscopic symmetry of a crystal is the intersection (the largest common subgroup) of the symmetry groups of its electric and magnetic structures:

$$G = G(\rho) \cap G(\boldsymbol{j}). \tag{70.4}$$

Symmetry group $G(\rho)$ of the electric charge density is simply Fedorov's, or space, group Φ of the crystal with the addition of time inversion, since the electric charge density is invariant with respect to time inversion: $G(\rho) = \Phi 1'$. However, the symmetry group $G(\boldsymbol{j})$ of the current density contains time inversion $1'$ if and only if $\boldsymbol{j}(\boldsymbol{r}) \equiv \equiv 0$, since time invesion reverses the direction of current. But if the crystal has magnetic structure ($\boldsymbol{j}(\boldsymbol{r}) \not\equiv 0$), $G(\boldsymbol{j})$ is one of the white or black-white Shubnikov groups. In this case related to the same type is group G of the crystal's microscopic symmetry.

For crystals without magnetic structure time inversion serves as one of the symmetry operations. And conversely, crystals which contain time inversion in their magnetic symmetry groups cannot have the magnetic structure. Such are the crystals relating to any of the 230 grey space groups of magnetic symmetry $\Phi 1'$. To these groups correspond point groups $G1'$ which are also grey. Thus, point groups of the magnetic symmetry of all crystals devoid of magnetic structure are grey. The converse is not true, however: a crystal with a grey point group can have a black-white space group; in this case it has the magnetic structure.

* Here and thereafter integration is done over an elementary cell; all the results are valid for any elementary volume which we imagine to consist of many whole-elementary cells.

It must be emphasized that in magnetic crystal physics a symmetry group of an ordinary non-magnetic crystal has notation different from that in classical crystal physics. So, rock salt crystals which possess no magnetic structure have classical symmetry $m3m$. the symmetry of quartz crystals is 32, of potassium dihydrophosphate — $\bar{4}2m$. But in magnetic crystal physics symmetry point groups of these crystals are $m3m1' = m3'm$, $321' = 3'2$ and $\bar{4}\ 2m1'$ respectively. The notation of their symmetry in magnetic crystal physics by $m3m$, 32 and $\bar{4}2m$ would be the gravest of errors: it would follow from this notation that the crystals have magnetic structure.

Ferromagnetic crystals have, as was already noted, non-zero magnetic moment $\boldsymbol{m}$. The vector of the magnetic moment $\boldsymbol{m}$ is axial and reverses its direction under time inversion. Hence its group of magnetic symmetry is ∞/mm'. Point groups of the symmetry of ferromagnetic crystals are subgroups of this group:

$$1,\ 2,\ 3,\ 4,\ 6,\ \bar{1},\ m,\ \bar{3},\ \bar{4},\ \bar{6},$$
$$2/m,\ 4/m,\ 6/m,\ 2',\ 22'2',\ 32',\ 42'2',$$
$$62'2',\ m',\ m'm'2,\ mm'2',\ 3m',\ 4m'm',$$
$$6m'm',\ \bar{3}m',\ \bar{4}2'm',\ \bar{6}m'2',\ 2'/m',$$
$$mm'm',\ 4/mm'm',\ 6/mm'm'.$$

In this list there are 31 groups of magnetic symmetry. Among them there are white groups (13) and black-white (18) ones, but no grey groups*.

The other 59 white and black-white point groups of magnetic symmetry can naturally be called antiferromagnetic point groups. Crystals with antiferromagnetic point groups are called *antiferromagnetics of type I*. Besides these, there are also *antiferromagnetics of type II* which are crystals with grey but no black-white space groups; their physical properties differ essentially from those of ferromagnetics of type I (see Sec. 73).

Table 70.1 shows the group distribution of crystals without magnetic structure, of ferromagnetics and antiferromagnetics of types I and II. It can also be seen from the Table that differences between grey groups, on the one hand, and white and black-white groups, on the other hand are physically essential. Distinctions between white and black-white groups, although highly important in the derivation of these groups, can be seen to have no physical meaning (see, however, Sec. 76).

Magnetic symmetry of crystals is revealed by means of the neutron diffraction analysis—the investigation of the diffraction of slow

* See also Tavger (1958) and Shuvalov (1959).

Table 70.1

Distribution of Crystals with Different Magnetic Properties by Magnetic Symmetry Groups

Space groups	Point groups		
	90 white and black-white groups		32 grey point groups
	31 ferromagnetic groups	59 antiferromagnetic groups	
1421 white and black-white groups	Ferromagnetics (275 Shubnikov's groups)	Antiferromagnetics of type I (629 Shubnikov's groups)	Antiferromagnetics of type II (517 Shubnikov's groups)
230 grey groups	—	—	Crystals without magnetic structure (230 Shubnikov's groups)

neutrons in crystal structure *: the diffraction of neutrons on nuclei is defined by group G (ρ), and the diffraction of neutrons on magnetic moments of electrons is defined by group $G(j)$. This method also allows revealing the space distribution of ordered magnetic moments in a crystal. The Fedorov group of a crystal is usually defined by X-ray diffraction analysis which is quite insensitive to the distribution of magnetic moments. It is important to understand the mutual interrelation of space groups determined by different methods.

Since the X-ray diffraction analysis does not enable one to distinguish antitranslation from ordinary translation, antirotation from ordinary rotation, it seems apparent that we can define by X-ray diffraction analysis the Fedorov group of a crystal with magnetic structure from its Shubnikov group by replacing all the crystal's antitranslations in the latter by ordinary translations, and all its antirotations by ordinary rotations. Thus we shall probably arrive at the very same Fedorov's group from which the Shubnikov group is derived (see Sec. 69).

In practice, however, the solution of this problem is much more complicated because of the relative weakness of magnetic interactions. Let us consider a concrete example. A ferromagnetic transition in crystals of iron (α-Fe) occurs at 1043 K—above this temperature the crystals are paramagnetic, below it they are ferromagnetic. The Shubnikov group of the paramagnetic phase is $Im3'm$, of the ferromagnetic phase it is $I4/mm'm'$. X-ray analysis of a monodomanial crystal should result, according to the above considerations,

* See Izyumov and Ozerov (1966).

in the Fedorov group $I4/mmm$. However, the crystallographic cell of the ferromagnetic phase, although it is, strictly speaking, a regular tetragonal prism, is practically undistinguishable from a cube: the axial ratio $c/a = 1 + 3 \cdot 10^{-5}$. Therefore the data of X-ray structure analysis give group $G(\rho) = Im3'm$. The distribution of magnetic moments in a crystallographic cell of a ferromagnetic crystal of iron is shown in Fig. 70.1, group $G(j) = I4/mm'm'$; the same is $G = G(\rho) \cap G(j)$. The point group of this crystal is $4/mm'm'$.

Figure 70.2 shows the distribution of magnetic moments in an antiferromagnetic crystal of manganese fluoride, MnF_2. Such a configuration of magnetic moments is characterized by Shubnikov's

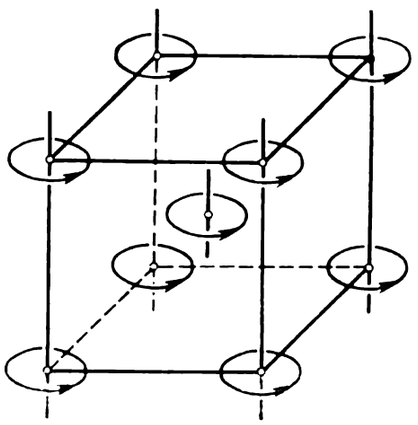


Fig. 70.1. Distribution of magnetic moments in a ferromagnetic iron crystal

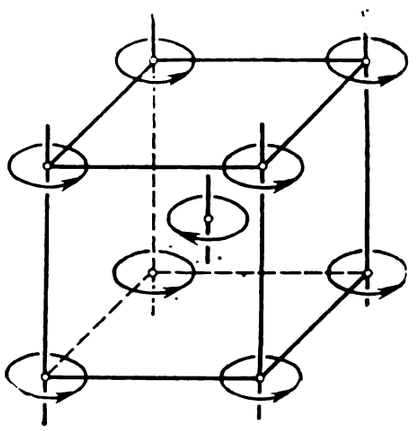


Fig. 70.2. Distribution of magnetic moments in an antiferromagnetic crystal of manganese fluoride

group $G(j) = P_I\, 4mnc$; on the other hand, according to the data of X-ray crystal-structure analysis $G(\rho) = P4/mnm1'$. The intersection of these groups is the Shubnikov group of antiferromagnetic manganese fluoride $P4'_2/mnm'$; correspondingly, the point group of this crystal's magnetic symmetry is $4'/mmm'$. Its physical properties corroborate this conclusion (see Sec. 73).

Along with uniaxial antiferromagnetics there also occur multiaxial ones; thus the Shubnikov group of dysprosium-aluminium garnet, $Dy_3Al_5O_{12}$, is $Ia3d'$, the point group of its magnetic symmetry is $m3m'$.

The symmetry of antiferromagnetics of type I, as was already noted, is characterized not only by black-white, but also by white point and space groups of magnetic symmetry. For instance, an antiferromagnetic crystal of chalcopyrite, $CuFeS_2$, is characterized by the Shubnikov group $I\bar{4}2d$ (and correspondingly by magnetic symmetry class $\bar{4}2m$).

Ilmenite, $FeTiO_2$, can serve as an example of an antiferromagnetic of type II; its Shubnikov group is the black-white $R_I\bar{3}$, and the magnetic symmetry class is grey $\bar{3}1'$.

With the aid of neutron diffraction there were also revealed such magnetic structures in which the array of magnetic moments, al-

though ordered, does not correspond to any of the 1421 white and black-white Shubnikov's groups, the so-called helical structures. Four types of such structures are known: a simple spiral *SS*, a ferromagnetic or conical spiral *FS*, a compound spiral *CS*, and, finally, a static longitudinal spin wave *LSW*; they are shown in Fig. 70.3. The simple spiral (*SS*) was found, for example, in holmium and dysprosium; the ferromagnetic spiral (*FS*) in holmium and erbium; the compound spiral (*CS*) and longitudinal spin wave (*LSW*), also in erbium: in different temperature ranges different types of magnetic ordering are realized. The symmetry of electric structure

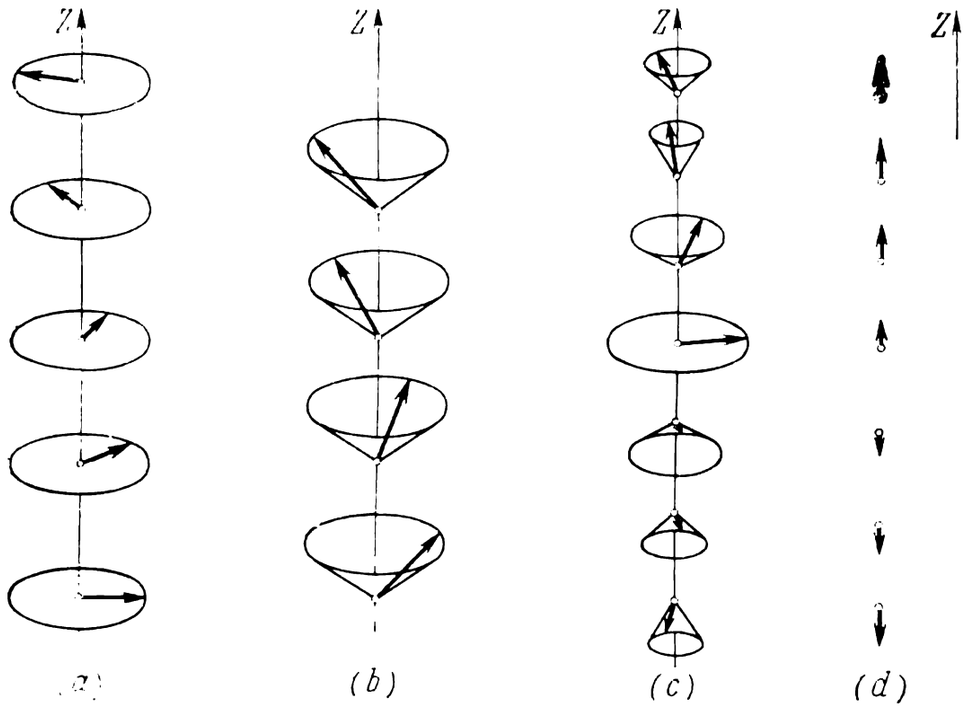


Fig. 70.3. Helical structures: (a) simple spiral, (b) ferromagnetic spiral, (c) compound spiral, (d) static longitudinal spin wave

G (ρ) in such crystals is simply one of Fedorov's groups (in many of them it is the group $P6_3/mmc$), complemented by time inversion, while the symmetry group of their magnetic structure G (j) is highly peculiar. In the planes perpendicular to the helicoid axis the group G (j) contains the same translations as the group G (ρ). But the traslation of the group G (ρ) directed along the helicoid axis is combined in the group G (j) with the rotation (*SS*, *FS* and *CS*) or with the alteration of the magnitude (*LSW*) of the magnetic moment. The angle of rotation connected with the elementary translation is not a divisor of a full rotation and, besides, it depends on temperature. Thus the magnetic moments of atoms in helical structures do not form a lattice, although the corresponding atoms do form it. This is also one of the consequences of the relative weakness of magnetic interactions. Symmetry groups describing such structures were de-

rived by Naisch (1963), the mechanism of their development, from the standpoint of Landau's theory of phase transitions of the second kind was investigated by Dzyaloshinsky (1964, 1964a).

Sec. 71. Geometric Realization of the Expanded Orthogonal Group

Axial vectors are invariant with respect to inversion, and, consequently, an axial vectorial basis has the same property (see Sec. 23). For this reason, to all orthogonal transformations of the axial vectorial basis there correspond orthogonal matrices $\| \overset{\circ}{c}_{i'k} \|$ with a positive determinant $\det \| \overset{\circ}{c}_{i'k} \| = 1$. Orthogonal matrices with a negative determinant correspond to no orthogonal transformations whatever.

Let us determine the action of time inversion $1'$ on axial vectors in the following manner: time inversion $1'$ reverses the circuit direction of all axial vectors. To this transformation there will correspond matrix $\|\overset{\circ}{c}_{i'k}(1')\| = -\delta_{i'k}$. Because of the invariance of axial vectors with respect to inversion, the space-time inversion (antiinversion) $\bar{1}'$ will have the same effect on all axial vectors, and the same matrix $\| \overset{\circ}{c}_{i'k}(\bar{1}') \| = -\delta_{i'k}$ will correspond to it. Generally, to all operations containing time inversion—to antioperations— there correspond orthogonal matrices $\| \overset{\circ}{c}_{i'k} \|$ with determinant $\det \| \overset{\circ}{c}_{i'k} \| = -1$.

The introduced definition has an obvious physical meaning: axial vectors thus determined coincide by their transformation properties with the magnetic field vector $\boldsymbol{H}$—they are also axial vectors reversing their sign with time inversion. It would be thus natural to ascribe to polar vectors the transformation properties of the electric field vector $\boldsymbol{E}$ which does not reverse its direction with time inversion. A polar vectorial basis constructed on polar vectors is also invariant with respect to time inversion. Therefore, under any—either simple or inversion—antirotations the polar vectorial basis is transformed by means of the same orthogonal matrix $\| c_{i'k} \|$ as under corresponding rotations.

Thus we have determined the law of the transformation of polar $(\boldsymbol{e}_i)$ and axial $(\overset{\circ}{\boldsymbol{e}}_i)$ base vectors under the action of any operation g contained in the expanded orthogonal group $\infty\infty\bar{1}1'$:

$$\begin{aligned} \boldsymbol{e}_{i'} &= c_{i'k}(g)\, \boldsymbol{e}_k, \\ \overset{\circ}{\boldsymbol{e}}_{i'} &= \overset{\circ}{c}_{i'k}(g)\, \overset{\circ}{\boldsymbol{e}}_k. \end{aligned} \tag{71.1}$$

To each operation $g \in \infty\infty\bar{1}1'$ there correspond two equal, or differing only by a sign, matrices $\|c_{i'k}(g)\|$ and $\|\overset{\circ}{c}_{i'k}(g)\|$. The expanded

orthogonal group contains four kinds of operations: proper rotations R, inversion rotations $\bar{1}R$, antirotations $1'R$ and inversion antirotations $\bar{1}'R$. If to the proper rotation R there corresponds matrix $\|r_{i'k}\|$, matrices $\|c_{i'k}(g)\|$ and $\|\overset{\circ}{c}_{i'k}(g)\|$ for any operation of the expanded orthogonal group are defined from the following table:

g	R	$\bar{1}R$	$1'R$	$\bar{1}'R$
$c_{i'k}$	$r_{i'k}$	$-r_{i'k}$	$r_{i'k}$	$-r_{i'k}$
$\overset{\circ}{c}_{i'k}$	$r_{i'k}$	$r_{i'k}$	$-r_{i'k}$	$-r_{i'k}$.

Having matched the polar and axial bases up to the coincidence of the corresponding vectors ($\boldsymbol{e}_1$ and $\overset{\circ}{\boldsymbol{e}}_1$, $\boldsymbol{e}_2$ and $\overset{\circ}{\boldsymbol{e}}_2$, $\boldsymbol{e}_3$ and $\overset{\circ}{\boldsymbol{e}}_3$), we obtain a combined basis. The matrix $\|c_{i'k}\|$ acts on its polar part, and $\|\overset{\circ}{c}_{i'k}\|$ on its axial part. Operations R rotate it as a whole, and it will therefore suffice to consider the action of inversions upon it.

Space inversion rotates the polar base vectors through angle π without changing the axial ones. Therefore, a right-hand triplet of polar vectors becomes a left-hand one, and a left-hand triplet becomes a right-hand one. Moreover, the sense of the screw formed by matched polar axial vectors is also reversed. Therefore, the combined basis which was consistent (inconsistent) prior to inversion persists under it (cf. Sec. 23).

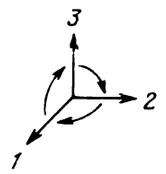
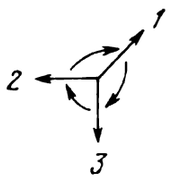
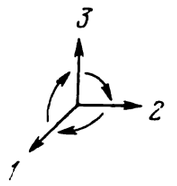
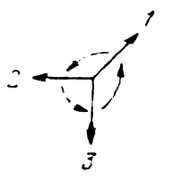
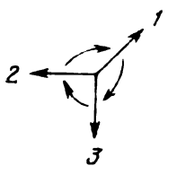
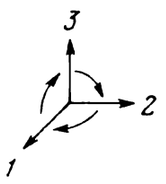
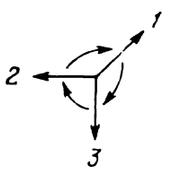
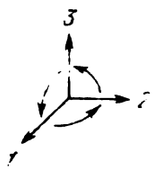
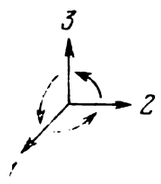
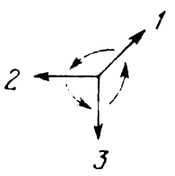
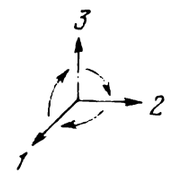
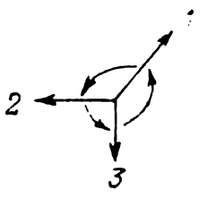
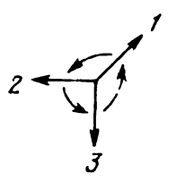
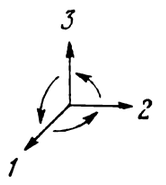
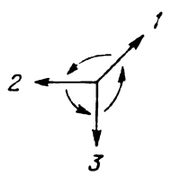
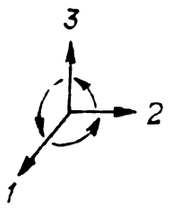
On the contrary, time inversion $1'$, reverses the circuit direction of axial base vectors without changing those of the axial ones. The triplet of polar vectors retains its handedness in the process, but the screws formed by the matched polar and axial vectors reverse their sense; thus a consistent basis becomes inconsistent, and vice versa.

Finally, the space-time inversion $\bar{1}'$ reverses both the directions of polar vectors and the circuit directions of axial vectors. Therefore a right-hand triplet of polar vectors becomes left-handed one, and a left-handed triplet, right-handed one, but the sense of the screw formed by the matched polar and axial vectors persists. As a result a consistent basis becomes inconsistent, and vice versa.

Table 71.1 shows the action of inversions on combined vectorial bases. The bases are called right- or left-handed depending on the polar base vectors forming a right- or a left-hand triplet. In right-handed consistent bases the polar and axial vectors form a right-handed screw, in the left-handed ones — a left-handed screw. Conversely, in inconsistent bases the sense of the screw is the opposite of that of the basis. A formal sign of the basis consistence is this: the circuit about the first base vector is done from the positive end of the second vector to the positive end of the third vector; the circuit directions about the other base vectors are derived therefrom by

Table 71.1

Action of Inversions on a Combined Vectorial Basis

Initial combined vectorial basis	The same basis after		
	space inversion $\bar{I}$	time inversion $\bar{I}'$	space-time inversion $\bar{I}'$
 right-handed consistent	 left-handed consistent	 right-handed inconsistent	 left-handed inconsistent
 left-handed consistent	 right-handed consistent	 left-handed inconsistent	 right-handed inconsistent
 right-handed inconsistent	 left-handed inconsistent	 right-handed consistent	 left-handed consistent
 left-handed inconsistent	 right-handed inconsistent	 left-handed consistent	 right-handed consistent

cyclic substitution. For inconsistent bases the circuit direction is opposite to the above.

Table 71.1 shows that different operations acting on a given basis transform it into bases that are likewise different. Thus, knowing the "old" and "new" combined bases we can unerringly tell by exactly what transformation the latter was obtained from the former.

Sec. 72. Tensors Defined on an Expanded Orthogonal Group

All tensors defined on the group of rotations undergo transformations of a single type, namely

$$A_{i_1' \ldots i_n'} = r_{i_1' k_1} \ldots r_{i_n' k_n} A_{k_1 \ldots k_n}. \tag{72.1}$$

Here $\|r_{i'k}\|$ is the matrix of rotations $R(\mathring{\boldsymbol{k}}, \varphi)$ about vector $\mathring{\boldsymbol{k}}$ by angle φ. But tensors defined on an orthogonal group are divided into two types. Under inversion rotation $\bar{1}R(\mathring{\boldsymbol{k}}, \varphi)$ of the reference frame, even-type tensors are transformed according to (72.1) while odd-type tensors are transformed according to formula

$$A_{i_1' \ldots i_n'} = -r_{i_1' k_1} \ldots r_{i_n' k_n} A_{k_1 \ldots k_n}. \tag{72.2}$$

Let us emphasize that $\|r_{i'k}\|$ is the matrix of the corresponding proper rotation $R(\boldsymbol{k}, \varphi)$ but not of the orthogonal transformation on the whole.

The expanded orthogonal group contains transformations of four kinds: proper rotations $R(\mathring{\boldsymbol{k}}, \varphi)$ and three kinds of improper ones, namely, inversion rotations $\bar{1}R(\mathring{\boldsymbol{k}}, \varphi)$, antirotations $1'R(\mathring{\boldsymbol{k}}, \varphi)$ and inversion antirotations $\bar{1}'R(\mathring{\boldsymbol{k}}, \varphi)$. The result of two consecutive improper rotations can be easily determined with the aid of the following multiplication table (Table 72.1) for the group of space-time inversions.

Table 72.1

Multiplication Table for Space-Time Inversions Group $\bar{1}1'$

	1	$\bar{1}$	$1'$	$\bar{1}'$
1	1	$\bar{1}$	$1'$	$\bar{1}'$
$\bar{1}$	$\bar{1}$	1	$\bar{1}'$	$1'$
$1'$	$1'$	$\bar{1}'$	1	$\bar{1}$
$\bar{1}'$	$\bar{1}'$	$1'$	$\bar{1}$	1

It can easily be shown that on an expanded orthogonal group there can be defined tensors of four types: of an even and three odd ones. The even-type tensors are invariant with respect to the inversion group $\bar{1}1'$; therefore under any transformation $JR(\mathring{k}, \varphi)$ where $J \in \bar{1}1'$, they are transformed according to (72.1). Tensors of all types are transformed according to this formula under proper rotations.

Every tensor of any odd type is transformed according to (72.2) under the action of improper rotations of two kinds, and according to (72.1) under the action of the third kind of rotation. Indeed, let a given tensor be transformed according to (72.2) under the action of inversion rotations. Under the action of antirotations it will be transformed either according to (72.1) or (72.2). Since an inversion antirotation can be regarded as the product of an inversion rotation and antirotation, it is apparent that in the first case the given tensor will be transformed according to (72.2) under the action of inversion antirotations, and in the second case, according to (72.1).

Having calculated all possibilities, we arrive at the conclusion that on an expanded orthogonal group exactly three types of odd tensors have been determined. The names of types (electric, magnetic, magnetoelectric) are related to the fact that to these types electric and magnetic fields vectors and the tensor of magnetoelectric polarization are respectively referred (see Sec. 73).

All tensors defined on an expanded orthogonal group are transformed according to relation

$$A_{i_1' \ldots i_n'} = \gamma r_{i_1' k_1} \ldots r_{i_n' k_n} A_{k_1 \ldots k_n}, \tag{72.3}$$

where the coefficient $\gamma = \pm 1$ depends on the type of tensor and the kind of transformation and is determined from the data of Table 72.2, while $\|r_{i'k}\|$ is the matrix of the corresponding proper rotation.

Table 72.2

Coefficients γ in Transformation Formula (72.3). The Tensor is Determined on an Expanded Orthogonal Group

Type of tensor	Kind of transformation			
	R	$\bar{1}R$	$1'R$	$\bar{1}'R$
Even	1	1	1	1
Electric	1	−1	1	−1
Magnetic	1	1	−1	−1
Magnetoelectric	1	−1	−1	1

The external symmetry of tensors determined on an expanded orthogonal group is determined by the maximum point group of magnetic symmetry with respect to which the given tensor is invariant. Table 72.3 shows the groups of magnetic symmetry of scalars and vectors of all four types.

Table 72.3

Magnetic Symmetry of Scalars and Vectors Determined on an Expanded Orthogonal Group

Type of tensor	Scalar	Vector
Even	$\infty\infty m1'$	$\infty/mm1'$
Electric	$\infty\infty 1'$	$\infty/m1'$
Magnetic	$\infty\infty m$	∞/mm'
Magnetoelectric	$\infty\infty m'$	$\infty/m'm$

Upon the comparison of the results of investigation of electric and magnetic quantities (see the end of Sec. 68) with this Table, we see that intensities of electric and magnetic fields are actually represented by vectors of the electric and magnetic types respectively. However, an electric charge is specified by a scalar of the even (not electric!) type. A magnetic charge, if it could have existed, would be specified by a scalar of the magnetoelectric type.

Let us consider the external symmetry of tensors of each type separately.

Even-type tensors transform under any improper rotations exactly in the same way as under corresponding proper rotations. Therefore, even-type matter tensors are the same for all classes of magnetic symmetry included in one subsystem. Generally, even-type matter tensors for crystals of all classes of magnetic symmetry differ from zero. On the contrary, matter tensors of any of the three odd types are identically zero for many classes of magnetic symmetry.

Electric-type tensors transform under any antirotations in the same way as under corresponding proper rotations, and under any inversion antirotations as under corresponding inversion rotations. Therefore, it is very easy to ascertain the form of an electric-type tensor invariant with respect to the specified point group of magnetic symmetry: it would suffice to cancel all the primes in the group notation and to find by a usual method (by the method of direct inspection or simply with the aid of tables) the form of a corresponding odd-type tensor invariant with respect to the obtained ordinary point group. Thus, the problem of the magnetic symmetry of electric-type tensors is immediately reduced to the problem of the ordinary symmetry of odd-type tensors.

Table 72.4

Correspondence Between Groups of Magnetic Symmetry of Tensors of Different Types

G	G_1	G_2
$\infty\infty m1'$ $\infty\infty m$ $\infty\infty m'$	$\infty\infty m1'$ $\infty\infty 1'$ $\infty\infty m'$	$\infty\infty m1'$ $\infty\infty m$ $\infty\infty 1'$
$\infty\infty 1'$ $\infty\infty$	$\infty\infty m$ $\infty\infty$	$\infty\infty m'$ $\infty\infty$
$m3'm$ $m3m$ $m3m'$ $m'3m'$ $m'3m$	$m3'm$ $43'2$ $\bar{4}3'm$ $m'3m'$ $m'3m$	$m3'm$ $m3m$ $m3m'$ $43'2$ $\bar{4}3'm$
$\bar{4}3'm$ $\bar{4}3m$ $\bar{4}3m'$	$m3m'$ $4'32'$ $4'3m'$	$m'3m$ $\bar{4}3m$ $4'32'$
$43'2$ 432 $4'32$	$m3m$ 432 $\bar{4}3m$	$m'3m'$ 432 $4'3m'$
$m3'$ $m3$ $m'3$	$m3'$ $23'$ $m'3$	$m3'$ $m3$ $23'$
$23'$ 23	$m3$ 23	$m'3$ 23
$\infty/mm1'$ ∞/mm $\infty/m'm$ ∞/mm' $\infty/m'm'$	$\infty/mm1'$ $\infty 21'$ $\infty/m'm$ $\infty m1'$ $\infty/m'm'$	$\infty/mm1'$ ∞/mm $\infty m1'$ ∞/mm' $\infty 21'$
$\infty m1'$ ∞m $\infty m'$	∞/mm' $\infty 2'$ $\infty m'$	$\infty/m'm$ ∞m $\infty 2'$
$\infty 21'$ $\infty 2$ $\infty 2'$	∞/mm $\infty 2$ ∞m	$\infty/m'm'$ $\infty 2$ $\infty m'$

G	G_1	G_2
$\infty/m1'$ ∞/m ∞/m'	$\infty/m1'$ $\infty 1'$ ∞/m'	$\infty/m1'$ ∞/m $\infty 1'$
$\infty 1'$ ∞	∞/m ∞	$\infty m'$ ∞
$6/mmm1'$ $6/mmm$ $6/m'mm$ $6/mm'm'$ $6/m'm'm'$ $6'/mmm'$ $6'/m'mm'$	$6/mmm1'$ $6221'$ $6/m'mm$ $6mm1'$ $6/m'm'm'$ $\bar{6}m21'$	$6/mmm1'$ $6/mmm$ $6mm1'$ $6/mm'm'$ $6221'$ $\bar{6}m21'$ $6'/m'mm'$
$\bar{6}m21'$ $\bar{6}m2$ $\bar{6}'m2'$ $\bar{6}m'2'$ $\bar{6}'m'2$	$6'/m'mm'$ $6'22'$ $6'm2$ $6'mm'$ $\bar{6}'m'2$	$6'/mmm'$ $\bar{6}m2$ $6'mm'$ $\bar{6}m'2'$ $6'22'$
$6mm1'$ $6mm$ $6m'm'$ $6'mm'$	$6/mm'm'$ $62'2'$ $6m'm'$ $\bar{6}m2'$	$6/m'mm$ $6mm$ $62'2'$ $\bar{6}'m2'$
$6221'$ 622 $62'2'$ $622'$	$6/mmm$ 622 $6mm$ $\bar{6}m2$	$6/m'm'm'$ 622 $6m'm'$ $\bar{6}'m'2$
$6/m1'$ $6/m$ $6/m'$ $6'/m$ $6'/m'$	$6/m1'$ $61'$ $6/m'$ $6'/m$ $\bar{6}1'$	$6/m1'$ $6/m$ $61'$ $\bar{6}1'$ $6'/m'$
$\bar{6}1'$ $\bar{6}$ $\bar{6}'$	$6'/m'$ $6'$ $\bar{6}'$	$6'/m$ $\bar{6}$ $6'$
$61'$ 6 $6'$	$6/m$ 6 $\bar{6}$	$6/m'$ 6 $\bar{6}'$

G	G_1	G_2
$4/mmm1'$ $4/mmm$ $4/m'mm$ $4/mm'm'$ $4/m'm'm'$ $4'/mmm'$ $4'/m'mm'$	$4/mmm1'$ $4221'$ $4/m'mm$ $4mm1'$ $4/m'm'm'$ $42m1'$ $4'/m'mm'$	$4/mmm1'$ $4/mmm$ $4mm1'$ $4/mm'm'$ $4221'$ $4'/mmm'$ $42m1'$
$\bar{4}2m1'$ $\bar{4}2m$ $\bar{4}2'm'$ $\bar{4}'2'm$ $\bar{4}'2m'$	$4'/mmm'$ $4'22'$ $4'mm'$ $\bar{4}'2'm$ $\bar{4}'2m'$	$4'/m'mm'$ $\bar{4}2m$ $\bar{4}2'm'$ $4'mm'$ $4'22'$
$4mm1'$ $4mm$ $4m'm'$ $4mm'$	$4/mm'm'$ $42'2'$ $4m'm'$ $\bar{4}2'm'$	$4/m'mm$ $4mm$ $42'2'$ $\bar{4}'2'm$
$4221'$ 422 $42'2'$ $4'22'$	$4/mmm$ 422 $4mm$ $42m$	$4/m'm'm'$ 422 $4m'm'$ $\bar{4}'2m'$
$4/m1'$ $4/m$ $4/m'$ $4'/m$ $4'/m'$	$4/m1'$ $41'$ $4/m'$ $\bar{4}1'$ $4'/m'$	$4/m1'$ $4/m$ $41'$ $4'/m$ $\bar{4}1'$
$\bar{4}1'$ $\bar{4}$ $\bar{4}'$	$4'/m$ $4'$ $\bar{4}'$	$4'/m'$ $\bar{4}$ $4'$
$41'$ 4 $4'$	$4/m$ 4 $\bar{4}$	$4/m'$ 4 $\bar{4}'$

G	G_1	G_2
$\bar{3}m1'$ $\bar{3}m$ $\bar{3}m$ $\bar{3}'m$ $\bar{3}'m'$	$\bar{3}m1'$ $3'2$ $3'm$ $\bar{3}'m$ $\bar{3}'m'$	$\bar{3}m1'$ $\bar{3}m$ $\bar{3}m'$ $3'm$ $3'2$
$3'm$ $3m$ $3m'$	$\bar{3}m'$ $32'$ $3m'$	$\bar{3}'m$ $3m$ $32'$
$3'2$ 32 $32'$	$\bar{3}m$ 32 $3m$	$\bar{3}'m'$ 32 $3m'$
$\bar{3}1'$ $\bar{3}$ $\bar{3}'$	$\bar{3}1'$ $3'$ $3'$	$\bar{3}1'$ $\bar{3}$ $3'$
$3'$ 3	$\bar{3}$ 3	$3'$ 3
$mmm1'$ mmm mmm' $mm'm$ $m'm'm'$	$mmm1'$ $2221'$ mmm' $mm21'$ $m'm'm'$	$mmm1'$ mmm $mm21'$ $mm'm'$ $2221'$
$mm21'$ $mm2$ $m'm'2$ $mm'2'$	$mm'm'$ $22'2'$ $m'm'2$ $mm'2'$	mmm' $mm2$ $22'2'$ $mm'2'$
$2221'$ 222 $22'2'$	mmm 222 $mm2$	$m'm'm'$ 222 $m'm'2$

Table 72.4 (cont'd)

G	G_1	G_2	G	G_1	G_2
$2/m1'$ $2/m$ $2/m'$ $2'/m$ $2'/m'$	$2/m1'$ $21'$ $2/m'$ $2'/m$ $m1'$	$2/m1'$ $2/m$ $21'$ $m1'$ $2'/m'$	$21'$ 2 $2'$	$2/m$ 2 m	$2/m'$ 2 m'
			$\bar{1}\bar{1}$ $\bar{1}$ $\bar{1}'$	$\bar{1}1'$ $1'$ $\bar{1}'$	$\bar{1}1'$ $\bar{1}$ $1'$
$m1'$ m m'	$2'/m'$ $2'$ m'	$2'/m$ m $2'$	$1'$ 1	$\bar{1}$ 1	$\bar{1}'$ 1

It is apparent that the form of an even-type tensor invariant with respect to the specified group of magnetic symmetry is determined in the same manner: we cancel all primes in the notation of the group and search for an even-type tensor invariant with respect to the obtained ordinary group.

Magnetic-type tensor, as can be seen from Table 72.2, is transformed under the action of antirotation $1'R\ (\mathring{\boldsymbol{k}}, \varphi)$ in the same way as an electric-type tensor under the action of a corresponding inversion rotation $\bar{1}R\ (\mathring{\boldsymbol{k}}, \varphi)$. Inversion antirotations $\bar{1}'R\ (\mathring{\boldsymbol{k}}, \varphi)$ produce the same effect on tensors of both types. Hence the following rule: a magnetic-type tensor invariant with respect to magnetic group G has exactly the same form as an electric-type tensor invariant with respect to magnetic group G_1. To obtain group G_1 from group G it is necessary to replace in the latter all inversion rotations by corresponding antirotations, and all antirotations, by inversion rotations.

The second rule is derived similarly: *magnetoelectric-type tensor* invariant with respect to magnetic group G has exactly the same form as the electric-type tensor invariant with respect to magnetic group G_2. To obtain group G_2 from group G it is necessary to replace in the latter all antirotations by corresponding inversion antirotations, and inversion antirotations, by simple antirotations.

Groups G_1 and G_2 for any specified group of magnetic symmetry are easily found with the aid of Table 72.4; the problem of the form of an electric-type tensor invariant with respect to the specified group of magnetic symmetry was discussed above. Thus, formal problems of magnetic crystal physics can be successfully reduced to the already solved problems of classical crystal physics (Sirotin, 1962; Birss, 1962).

Sec. 73. Piezomagnetic and Magnetoelectric Effects

If three components of the magnetic field vector H_k are included among generalized thermodynamic forces X_B (see Sec. 57), and the three components of the magnetic induction vector divided by 4π, $\widetilde{B}_i = (1/4\pi)\, B_i$ are included among generalized thermodynamic coordinates x_A, then the order of the thermodynamic matrix will rise to 13. Then the relation between generalized thermodynamic coordinates and generalized thermodynamic forces in a linear approximation will appear as (cf. expressions (57.18))

$$\Sigma = (C_p/T)\,\Theta + p_k E_k + q_k H_k + \alpha_\mu \sigma_\mu, \tag{73.1a}$$

$$\widetilde{D}_i = p_i \Theta + (1/4\pi)\,\varkappa_{ik} E_k + (1/4\pi)\,\nu_{ik} H_k + d_{i\mu}\sigma_\mu, \tag{73.1b}$$

$$\widetilde{B}_i = q_i \Theta + (1/4\pi)\,\nu_{ki} E_k + (1/4\pi)\,\mu_{ik} H_k + b_{i\mu}\sigma_\mu. \tag{73.1c}$$

$$\varepsilon_\lambda = \alpha_\lambda \Theta + d_{k\lambda} E_k + b_{k\lambda} H_k + s_{\lambda\mu}\sigma_\mu. \tag{73.1d}$$

Formulas (73.1) contain, along with the known matter tensors, some new ones which describe the effects we have not considered yet. The essence of these effects is easily understood by analogy with the corresponding electric effects. Thus, coefficients q_i evidently characterize the *pyromagnetic effect* and its converse *linear magnetocaloric* effect, and taken together represent the vector of pyromagnetic coefficients **q**. Coefficients $b_{i\mu}$ describe the *direct* and *converse piezomagnetic effects*; taken together they constitute a third-rank tensor symmetric with respect to two indices, i.e. the tensor of piezomagnetic coefficients **b**. Finally, coefficients μ_{ik} constitute a symmetric second-rank tensor, i.e. the tensor of magnetic permeability $\boldsymbol{\mu}$.

Coefficients ν_{ik} have no analogue. They specify the *direct* and *converse magnetoelectric effects*: crystals with these coefficients differing from zero are polarized, when placed in a magnetic field (direct effect), and magnetized when placed in an electric field (converse effect). All these coefficients together constitute an asymmetric second-rank tensor $\boldsymbol{\nu}$ which is the tensor of magnetoelectric coefficients.

Let us take from (73.1) the terms containing new matter tensors and note the types of tensor quantities connected by them. We shall obtain

$$\boldsymbol{\Sigma} = \boldsymbol{q}\cdot\boldsymbol{H} + \ldots \text{ (even)} = \boldsymbol{q}\cdot\text{(magnetic)},$$

$$\widetilde{\boldsymbol{D}} = \boldsymbol{\nu}\cdot\boldsymbol{H} + \ldots \text{ (electric)} = \boldsymbol{\nu}\cdot\text{(magnetic)},$$

$$\widetilde{\boldsymbol{B}} = \boldsymbol{E}\cdot\boldsymbol{\nu} + \ldots \text{ (magnetic)} = \text{(electric)}\cdot\boldsymbol{\nu},$$

$$\widetilde{\boldsymbol{B}} = \boldsymbol{\mu}\cdot\boldsymbol{H} + \ldots \text{ (magnetic)} = \boldsymbol{\mu}\cdot\text{(magnetic)},$$

$$\widetilde{\boldsymbol{B}} = \mathbf{b} : \boldsymbol{\sigma} + \ldots \text{ (magnetic)} = \mathbf{b} : \text{(even)},$$

$$\boldsymbol{\varepsilon} = \boldsymbol{H}\cdot\mathbf{b} + \ldots \text{ (even)} = \text{(magnetic)}\cdot\mathbf{b},$$

whence each of the types of matter tensors we are concerned with becomes apparent: $\boldsymbol{q}$ is the magnetic type, **b** is the magnetic type, $\boldsymbol{\mu}$ is the even type, $\boldsymbol{\nu}$ is the magnetoelectric type.

The form of each of these tensors for any class of magnetic symmetry can be found without any trouble by the methods described in Sec. 72. We shall merely mention here the classes in which the effects specified by these tensors are possible.

The *pyromagnetic effect* is specified by matter vector $\boldsymbol{q}$ of the magnetic type. Obviously, this vector does not become identically zero only in those crystals whose magnetic symmetry groups are the subgroups of the symmetry groups

of the magnetic-type vector ∞/mm'. These are the already known point groups of ferromagnetics; they were listed in Sec. 70.

The *piezomagnetic effect* is specified by tensor **b**. This is a third-rank magnetic-type tensor, symmetric with respect of the last two indices. Like all magnetic-type tensors it vanishes in crystals whose symmetry groups contain time inversion or antiinversion, but not only in these crystals. The point is that the tensor of piezomagnetic coefficients is similar to the tensor of piezoelectric coefficients. The latter, as we know from classical (non-magnetic) crystal physics, becomes zero not only in centrosymmetric crystals, but also in crystals of class 432. Hence (see Table 72.4), it vanishes in crystals of magnetic classes $43'2$, $4'32'$ and 432. By the substitution, with the aid of the same Table of inversion rotations for antirotations we shall obtain magnetic classes $m3m$, $\bar{4}3m$ and 432, in which the tensor of piezomagnetic coefficients evidently becomes zero.

The *magnetoelectric effect* is specified by a second-rank tensor **v** of the magnetoelectric type which is, generally, non-symmetric. Like all magnetoelectric-type tensors it vanishes in crystals whose magnetic symmetry groups contain time inversion or the ordinary (space) inversion. The tensor of magnetoelectric coefficients is similar to the full (non-symmetric) tensor of optical activity. The latter is known to vanish (see Tables 47.1 and E.9) not only in centrosymmetric crystals, but also in crystals of classes $\bar{4}3m$, $\bar{6}m2$, and $\bar{6}$, and hence in crystals of the magnetic classes $\bar{4}3'm$, $\bar{4}3m$, $\bar{4}'3m'$, $\bar{6}m21'$, $\bar{6}m2$, $\bar{6}'m2'$, $\bar{6}m'2'$, $\bar{6}'m'2$, $\bar{6}1'$, 6 and $\bar{6}'$. The substitution in these classes of all antirotations by the corresponding inversion antirotations, and of inversion antirotations by simple antirotations will give us the magnetic classes $m3m'$, $\bar{4}3m$, $\bar{4}'32'$, $6'/mmm'$, $\bar{6}m2$, $6'mm'$, $\bar{6}m'2'$, $6'22'$, $6'/m$, $\bar{6}$ and $6'$; in crystals of the listed classes there can be no magnetoelectric effect.

Using the same analogy it can be easily shown that in crystals of the magnetic classes $m'3m'$, 432, $\bar{4}'3m'$, $m'3$, and 23 the tensor of magnetoelectric coefficients is isotropic. It follows that whatever is the direction of the magnetic field, a crystal of one of those classes placed in it will be polarized in the same direction. And conversely, such a crystal placed in an electric field of any sense will be magnetized in the same direction.

It can also be concluded from this analogy that in textures of magnetic classes $\infty/m'm$, ∞m, $\infty 2'$, and correspondingly in crystals of magnetic classes $6/m'mm$, $6mm$, $62'2'$, $4/m'mm$, $4mm$, $42'2'$, $3m$, $32'$, as well as $\bar{6}'m2'$, $\bar{4}'2'm$, and $\bar{3}'m$ the tensor of magnetoelectric coefficients is antisymmetric. Such crystals placed in a magnetic (or electric) field are polarized (or magnetized) in a direction perpendicular to the field. It would be most convenient to direct the field perpendicularly to the principal symmetry axis of the crystal; the polarization (or magnetization) is also perpendicular to this axis.

The tensors of piezomagnetic and magnetoelectric effects reverse their signs under the action of time inversion and consequently are identically zero in all crystals that do not possess magnetic structure. Until the concept of magnetic symmetry was introduced into physics, it had been believed that the symmetry of the piezomagnetic effect differed from that of the piezoelectric effect only due to vectors, characterizing a magnetic field, being axial, and vectors, characterizing an electric field, being polar. It had been therefore assumed that the internal symmetry of the tensor of piezomagnetic coefficients had been $\varepsilon V\,[V^2]$, whence there had been calculated the general form of this tensor for all crystallographic classes (see Table E.14). Insofar as for all classes of them with the exception of three ($m3m$, 432, and $\bar{4}3m$) this tensor differs from zero, there had been made numerous attempts to reveal the piezomagnetic structure; naturally, all these attempts had failed. Only when Dzyaloshinsky showed (1957, 1959) that piezomagnetic and magnetoelectric effects could be found only in crystals possessing magnetic structure and named some crystals whose magnetic symmetry admitted

these effects, Borovik-Romanov (1959, 1960) revealed the piezomagnetic effect in crystals of CoF_2 and MnF_2, while Astrov (1960) found the magnetoelectric effect in crystals of Cr_2O_3.

The availability of magnetic structure in a crystal is a necessary but not a sufficient condition for the manifestation in this crystal of the effects specified by tensors of the magnetic or magnetoelectric type. If a crystal has magnetic structure, it can be stated that its space group contains no time inversion (is not "grey"). For matter tensors of magnetic and magnetoelectric type not to become identically zero, it is necessary for the point group of the magnetic symmetry of the crystal not to contain time inversion (not to be grey). This is a much more rigorous requirement; it is not met by crystals called the antiferromagnetics of type II (Sec. 70) (i.e. crystals containing antitranslations in their Shubnikov group). Thus, the effects determined by tensors of magnetic and magnetoelectric types are impossible not only in crystals without magnetic structure, but also in antiferromagnetics of type II.

On the problems mentioned in this chapter see K. P. Belov (1959); K. P. Belov, Belyanchikova et al. (1965); Vonsovsky (1971); Izyumov and Ozerov (1966); Koptsik (1966, 1967); Landau and Lifshits (1957); Turov (1963); Shubnikov (1951); Shubnikov and Koptsik (1972); Birss (1964); Bhagavantam (1966).

Chapter IX

EFFECTS OF THE HIGHER ORDERS

Sec. 74. Thermodynamic Consideration of Non-Linear Effects

Within the framework of thermodynamics of crystals (see Secs 57, 60, 61, 63) non-linear effects can be described with account taken of terms of the third degree in the expansions of thermodynamic potentials. So, for the thermodynamic potential Φ and isothermal processes ($\Theta = 0$), instead of (60.8) the following expansion should be used

$$\Phi = \Phi_0 + \frac{1}{2}\left(\frac{\partial^2\Phi}{\partial X_a\,\partial X_b}\right)_0 X_a X_b + \frac{1}{6}\left(\frac{\partial^3\Phi}{\partial X_a\,\partial X_b\,\partial X_c}\right)_0 X_a X_b X_c$$
$$(a,\ b,\ c = 1,\ \ldots,\ 9)$$

where X_a are the components of the electric field vector $\boldsymbol{E}$ and the stress tensor σ. Taking expressions (57.13), (57.14) and (57.17) into consideration and using for the third derivatives of the thermodynamic potential notation

$$\begin{aligned} R_{ijk} &= -\frac{1}{2}\left(\frac{\partial^3\Phi}{\partial E_i\,\partial E_j\,\partial E_k}\right)_0, & P_{ij\lambda} &= -\frac{1}{2}\left(\frac{\partial^3\Phi}{\partial E_i\,\partial E_j\,\partial \sigma_\lambda}\right)_0, \\ Q_{i\lambda\mu} &= -\frac{1}{2}\left(\frac{\partial^3\Phi}{\partial E_i\,\partial \sigma_\lambda\,\partial \sigma_\mu}\right)_0, & L_{\lambda\mu\nu} &= -\frac{1}{2}\left(\frac{\partial^3\Phi}{\partial \sigma_\lambda\,\partial \sigma_\mu\,\partial \sigma_\nu}\right)_0, \end{aligned} \tag{74.1}$$

we write this expansion as follows

$$\Phi = \Phi_0 - \frac{1}{2}\tilde{\varkappa}_{ij}E_iE_j - d_{i\lambda}E_i\sigma_\lambda - \frac{1}{2}s_{\lambda\mu}\sigma_\lambda\sigma_\mu - \frac{1}{3}R_{ijk}E_iE_jE_k -$$
$$- P_{ij\lambda}E_iE_j\sigma_\lambda - Q_{i\lambda\mu}E_i\sigma_\lambda\sigma_\mu - \frac{1}{3}L_{\lambda\mu\nu}\sigma_\lambda\sigma_\mu\sigma_\nu. \tag{74.2}$$

According to (57.7) we now obtain for the electric induction vector $\boldsymbol{D}$ and the small strains tensor ε the generalization of relations (57.18)

$$\tilde{D}_i = \tilde{\varkappa}_{ij}E_j + d_{i\lambda}\sigma_\lambda + \tilde{R}_{ijk}E_jE_k + 2P_{ij\lambda}E_j\sigma_\lambda + Q_{i\lambda\mu}\sigma_\lambda\sigma_\mu, \tag{74.3a}$$

$$\varepsilon_\lambda = d_{i\lambda}E_i + s_{\lambda\mu}\sigma_\mu + P_{ij\lambda}E_iE_j + 2Q_{i\lambda\mu}E_i\sigma_\mu + L_{\lambda\mu\nu}\sigma_\mu\sigma_\nu; \tag{74.3b}$$

as in Ch. VII the tilde means division by 4π.

Instead of coefficients $P_{ij\lambda}$, $Q_{i\lambda\mu}$, $L_{\lambda\mu\nu}$ in relations for $\tilde{D}$ and ε the components of the corresponding matter tensors can be used:

$$\tilde{D}_i = \tilde{\varkappa}_{ij}E_j + d_{ijk}\sigma_{jk} + \tilde{R}_{ijk}E_jE_k + 2P_{ijkl}E_j\sigma_{kl} + Q_{ijklm}\sigma_{jk}\sigma_{lm}, \tag{74.4a}$$

$$\varepsilon_{ij} = d_{kij}E_k + s_{ijkl}\sigma_{kl} + P_{kij}E_kE_l + 2Q_{kijlm}E_k\sigma_{lm} + L_{ijklmn}\sigma_{kl}\sigma_{mn}. \tag{74.4b}$$

The internal symmetry and the names of these tensors are as follows:

Tensor	Symmetry	Name
R	$[V^3]$	tensor of quadratic coefficients of dielectric permittivity,
P	$[V^2]^2$	tensor of coefficients of electrostriction,
Q	$V[[V^2]^2]$	tensor of quadratic piezoelectric coefficients,
L	$[[V^2]^3]$	tensor of quadratic coefficients of elastic compliance *

The recalculation rules connecting components of these tensors with coefficients $P_{ij\lambda}$, $Q_{i\lambda\mu}$ and $L_{\lambda\mu\nu}$ are given in Appendix F. The external symmetry of these tensors, as of any matter tensors, is not lower than that of the crystal; their general form for different classes is given in Appendix E (see also Sec. 48).

Tensors **P** and **L** are of the even type; they differ from zero for all symmetry classes of crystals. Quadratic coefficients of elastic compliance describe small corrections to Hooke's law. As for the coefficients of electrostriction, they describe small corrections to the converse piezoelectric effect in piezoelectric crystals, while for crystals of non-piezoelectric classes and for isotropic bodies all strain caused by the action of an electric field on a crystal reduces to electrostriction.

Tensors **R** and **Q** are of the odd type. Tensors **Q** survive for crystals of all non-centrosymmetric classes. In particular, in crystals of class 432 in which the ordinary linear piezoelectric effect is impossible, there could be observed the quadratic piezoelectric effect: electric polarization under the action of mechanical stresses, proportional, however, not to the components of the stress tensor but to some of their paired products. Tensors of the quadratic coefficients of dielectric permittivity **R** differ from zero only in crystals whose symmetry permits the longitudinal piezoelectric effect; the general form of such

* Different definitions of these tensors can be found in literature, and in particular, the coefficient 1/2 in formulas (74.1) is sometimes absent; it is implied in this case, of course, that the coefficient 1/2 appears in (74.2)-(74.4). Exactly so tensors $g_{\lambda\mu\varkappa}$ and $c_{\lambda\mu\nu}$ were determined in (74.5)-(74.8).

tensors is given in Table E. 10, and the symmetry classes of this effect in Table 58.3.

That the influence of mechanical stresses on dielectric permittivity in (74.3a) and (74.4a) is described by the same coefffcients which describe electrostriction in (74.3b) and (74.4b) results from the fact that these coefficients are the third derivatives of the thermodynamic potential (see 74.1). For the same reason the coefficients of the quadratic piezoelectric effect also characterize the influence of an electric field on coefficients of elastic compliance.

The possibility of even an approximate application of thermodynamic considerations for diminishing the number of independent coefficients should be borne in mind when the effects of the higher orders are analyzed. For example, propagation of elastic waves in a crystal subjected to static stress σ^{st}, considerably exceeding stresses connected with the elastic wave, is determined by coefficients of elasticity

$$c_{\lambda\mu} = c_{\lambda\mu}^{(0)} + g_{\lambda\mu\varkappa}\sigma_{\varkappa}^{st}, \tag{74.5}$$

where $c_{\lambda\mu}^{(0)}$ are the elasticity coefficients of an unstressed crystal*. Coefficients $g_{\lambda\mu\varkappa}$ are the components of a tensor with internal symmetry $[[V^2]^2]$ $[V^2]$ which in a general case has 126 independent components. Let us consider, however, the elastic energy of a crystal up to terms cubic with regard to strain

$$W = \frac{1}{2} c_{\lambda\mu}^{(0)}\varepsilon_\lambda\varepsilon_\mu + \frac{1}{6} C_{\lambda\mu\nu}\varepsilon_\lambda\varepsilon_\mu\varepsilon_\nu. \tag{74.6}$$

Apparently, $C_{\lambda\mu\nu} = \partial^3 W/\partial\varepsilon_\lambda\partial\varepsilon_\mu\partial\varepsilon_\nu$ are the components of a tensor with internal symmetry $[[V^2]^3]$ which generally has, according to Tables 47.1a and 47.1b, 56 independent components. Having twice differentiated elastic energy (74.6) with respect to strains, we find

$$c_{\lambda\mu} = \frac{\partial^2 W}{\partial\varepsilon_\lambda\,\partial\varepsilon_\mu} = c_{\lambda\mu}^{(0)} + C_{\lambda\mu\nu}\varepsilon_\nu, \tag{74.7}$$

where ε_ν can be obviously considered to be ε_ν^{st}. With the degree of accuracy here adopted $\varepsilon_\nu^{st} = s_{\nu\varkappa}\sigma_\varkappa^{st}$, where $s_{\nu\varkappa}$ is the coefficient of elastic compliance, and consequently $c_{\lambda\mu} = c_{\lambda\mu}^{(0)} + C_{\lambda\mu\nu}s_{\nu\varkappa}\sigma_\varkappa^{st}$. Comparing this with (74.5), we obtain

$$g_{\lambda\mu\varkappa} = C_{\lambda\mu\nu}s_{\nu\varkappa}. \tag{74.8}$$

Relation (74.8) is not at variance with the fact of the internal symmetry of tensor g being $[[V^2]^2]$ $[V^2]$, but it sharply decreases the number of independent components of this tensor, from 126 to 56 +

* On propagation of elastic waves under these conditions and on other problems of non-linear crystal acoustics see Thurston (1964); Zarembo and Krasilnikov (1970).

$+ 21 = 77$, only 56 of them characterizing non-linear elastic properties. In the derivation of (74.8) no account was taken of the difference between the isothermal and adiabatic coefficients; taking this difference into consideration in the determination of the principal term, i.e. $c_{\lambda\mu}^{(0)}$, we can evidently neglect it in the assessment of small increments of the term.

The form of tensors $C_{\lambda\mu\nu}$ and $g_{\lambda\mu\nu}$ for several classes is given in Tables E. 24 and E. 25. Work is being done on the experimental determination of other similar tensors too, e.g. of the tensor of the quadratic piezoelectric effect and the fifth-rank tensor determining the strain component which depends on the electric field intensity cube: $\varepsilon_{ij}^{(3)} = \lambda_{ijklm} E_k E_l E_m$.

Sec. 75. Piezoresistive Effect

The piezoresistive (tensoresistive) effect consists in the variation of the electrical resistance of a material under the action of mechanical stresses (or strains). The piezoresistive effect is found in many substances, including metals, but it is exhibited to the greatest extent by semiconductors, this allowing the use of semiconducting materials: Ge, Si, GaSb, InSb, PbTe, Bi_2Te_3, for the manufacture of highly sensitive strain gauges, i.e. instruments that transform mechanical strains (stresses) into electrical quantities.

The piezoresistive effect can be represented as a change of the tensor of specific resistance ρ_{il} under the action of stresses σ_{mn}:

$$E_i = (\rho_{il}^0 + P_{ilmn}\sigma_{mn})\, j_l; \tag{75.1}$$

here E is the electric field intensity, j is the current density, ρ_{il}^0 is the tensor of the specific resistance of the crystal in the absence of mechanical stresses. More often, however, piezoresistive properties of a crystal are characterized by the tensor of piezoresistive coefficients Π_{klmn} which is connected with tensor P_{ilmn} by the relation

$$P_{ilmn} = \rho_{ik}^0 \Pi_{klmn} \tag{75.2}$$

the equation of the piezoresistive effect becoming in this case

$$E_j = \rho_{ik}^0 (\delta_{kl} + \Pi_{klmn}\sigma_{mn})\, j_l. \tag{75.3}$$

In crystals of the cubic system, i.e. in the majority of semiconductor crystals used as tensoresistors, $\rho_{ik}^0 = \rho^0 \delta_{ik}$ and

$$E_i = \rho^0 (\delta_{kl} + \Pi_{klmn}\sigma_{mn})\, j_l. \tag{75.4}$$

Another aspect of the piezoresistive effect—the dependence of the specific resistance of a crystal on strain ε_{pq}—is characterized by the equation

$$E_i = \rho_{ik}^0 (\delta_{kl} + m_{klpq}\varepsilon_{pq})\, j_l; \tag{75.5}$$

the tensor of elastoresistive coefficients $\mathbf{m}$ is connected with tensor $\mathbf{\Pi}$ by relations that follow from Hooke's law

$$m_{klpq} = \Pi_{klmn} c_{mnpq}, \quad \Pi_{klmn} = m_{klpq} s_{pqmn}, \tag{75.6}$$

in which c_{mnpq} are the elasticity coefficients, s_{pqmn} are elastic compliance coefficients.

The internal symmetry of tensors of piezoresistive and elastoresistive coefficients is $[V^2]^2$; in accordance with the symmetry of tensors ρ_{kl}, σ_{mn}, and ε_{pq} with respect to indices the former are symmetric with respect to the first two and the second two indices, for example

$$\Pi_{klmn} = \Pi_{lkmn} = \Pi_{klnm} = \Pi_{lknm}. \tag{75.7}$$

These tensors can also be written with two indices: $\Pi_{\lambda\mu}$ is usually connected with Π_{klmn} by the relation

$$\Pi_{\lambda\mu} = \begin{cases} \Pi_{klmn} & (kl \leftrightarrow \lambda = 1, \ldots, 6;\ mn \leftrightarrow \mu = 1, 2, 3), \\ 2\Pi_{klmn} & (kl \leftrightarrow \lambda = 1, \ldots, 6;\ mn \leftrightarrow \mu = 4, 5, 6) \end{cases}$$

(the relation connecting $P_{\lambda\mu}$ with P_{klmn} is the same), while $m_{\lambda\nu}$ is connected with m_{klpq} by the relation

$$m_{\lambda\nu} = m_{klpq} \quad (kl \leftrightarrow \lambda = 1, \ldots, 6;\quad pq \leftrightarrow \nu = 1, \ldots, 6);$$

(75.6) then takes the form

$$m_{\lambda\nu} = \Pi_{\lambda\mu} c_{\mu\nu}, \qquad \Pi_{\lambda\mu} = m_{\lambda\nu} s_{\nu\mu}. \tag{75.8}$$

The general form of tensors with such internal symmetry is given for all crystallographic and limit classes in Table E.19.

When the piezoresistive effect is used in practice, the potential difference U in the direction of the unit vector $\boldsymbol{u}$, and the current intensity I are measured. Then current density $j = (I/S)\,\boldsymbol{q}$, where $\boldsymbol{q}$ is the unit vector of the current direction, and S is the area of the tensoresistor cross-section. Since $U = aE\cdot u$, where a is the base of the potential difference measurement, we obtain from equation (75.3)

$$U = (aI/S)\,\rho^0_{ik} u_i\,(\delta_{kl} + \Pi_{klmn}\sigma_{mn})\,q_l. \tag{75.9}$$

For instance, if the potential difference is measured in the direction of current, vectors $\boldsymbol{u}$ and $\boldsymbol{q}$ coincide; for crystals with isotropic electric resistance this gives

$$U = (\rho^0 aI/S)\,(1 + \Pi_{klmn} q_k q_l \sigma_{mn}). \tag{75.10}$$

It may be preferable for the potential difference to be proportional to mechanical stresses and to vanish in their absence. In case of isotropic electric resistance this requirement calls for the vectors $\boldsymbol{u}$ and $\boldsymbol{q}$ to be mutually perpendicular; then

$$U = (\rho^0 aI/S)\,\Pi_{klmn} u_k q_l \sigma_{mn} \quad (u_i q_i = 0) \tag{75.11}$$

(in a general case the directions of $\boldsymbol{u}$ and $\boldsymbol{q}$ are chosen so that $\rho^0_{ik} u_i q_k = 0$).

For making these formulas still more concrete it is necessary to know the orientation of mechanical stresses with respect to the direction of current and the direction of the potential difference measurement. Thus, in case of the coincidence of the directions of current, the potential difference measurement and the uniaxial stress $\sigma = \sigma\boldsymbol{qq}$ we have the longitudinal piezoresistive effect equal to

$$U = (\rho^0 aI/S)\,(1 + \sigma\Pi_{klmn} q_k q_l q_m q_n), \tag{75.12}$$

while for the case of the mutual perpendicularity of the vectors $\boldsymbol{u}$ and $\boldsymbol{q}$ and the coincidence of the uniaxial stress with one of them (say, with $\boldsymbol{q}$), we have

$$U = (\rho^0 aI/S)\,\sigma\Pi_{klmn} u_k q_l q_m q_n \quad (u_i q_i = 0). \tag{75.13}$$

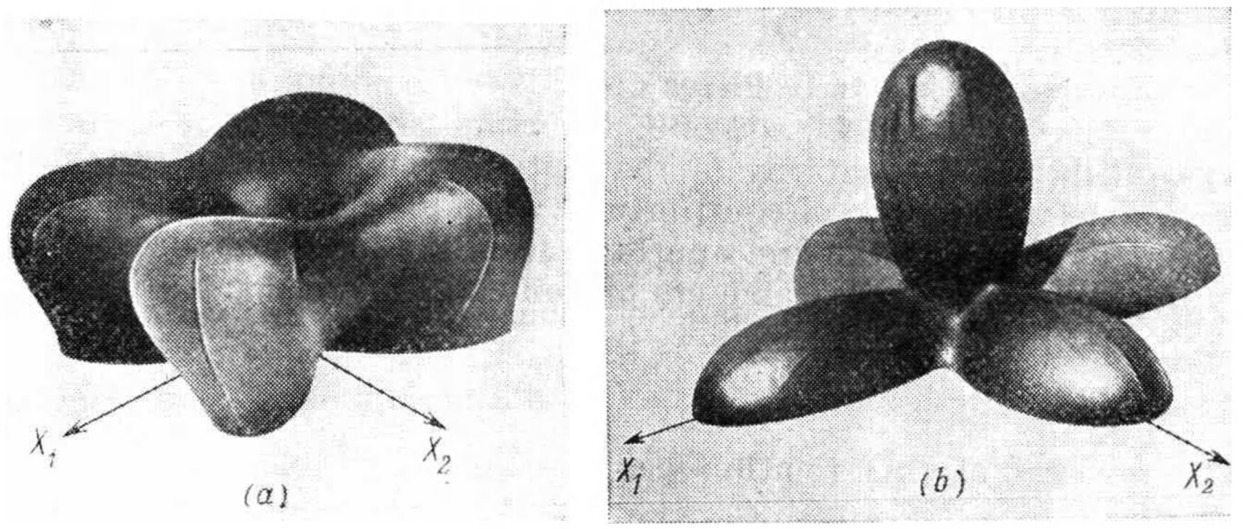


Fig. 75.1. Models of the representation surfaces of the longitudinal piezoresistive effect in silicon crystals (class $m3m$): (a) n-type crystal, $\rho = 11.7\Omega\cdot$cm; (b) p-type crystal, $\rho = 7.8\ \Omega\cdot$cm. Only the upper halves of the surfaces are shown, the lower halves being their mirror reflections (Butabayev and Smyslov, 1971)

The anisotropy of piezoresistive properties of semiconductor crystals is highly pronounced, this being evident from the representation surfaces of the longitudinal piezoresistive effect (Fig. 75.1).

For more detailed information on the physics of the piezoresistive effect and its uses see Mason (1964); Thurston (1967); Mason (1966); Bier and Pikus (1972).

Sec. 76. Onsager Reciprocal Relations and Thermogalvanomagnetic Effects

In the thermodynamics of irreversible processes an important role is played by the Onsager reciprocal relations*. Let the divergence of a system from equilibrium be characterized by parameters ξ_a which vanish in the state of equilibrium. The system returns to the state of equilibrium at a rate characterized in these terms by the derivatives $-\dot{\xi}_a$. The rate is apparently the higher, the greater the divergence of the system from equilibrium, and in the first approximation it linearly depends on the divergence:

$$-\dot{\xi}_a = A_{ab}\xi_b. \tag{76.1}$$

In thermodynamics of irreversible processes the quantities $J_a = -\dot{\xi}_a$ are called *fluxes*, and quantities

$$K_a = -\frac{\partial S}{\partial \xi_a}, \tag{76.2}$$

* See de Groot and Mazur (1962); Haase (1963); Landau and Lifshits (1954, Sec. 58; 1957, Sec. 25; 1976, Sec. 33).

where S is the entropy, are called *forces conjugate to the corresponding fluxes**.

The forces conjugate to fluxes also differ from zero only insofar as the system is not in the state of equilibrium, since with the approach to equilibrium the entropy of the system increases and attains its maximum in the state of equilibrium: when all $\xi_a = 0$, all $\partial S/\partial \xi_b = 0$. Obviously, in the first approximation the forces are also linearly dependent on the parameters of non-equilibrium ξ_b:

$$K_a = B_{ab}\xi_b.$$

The reversal of this relation has the form

$$\xi_b = C_{bc}K_c,$$

where C is a quadratic matrix reciprocal of matrix B:

$$C_{bc}B_{ca} = \delta_{ba}.$$

The fluxes and forces conjugate to them are directly related to the rate of the increase of entropy in the course of the system's approach to equilibrium. Indeed

$$\left(\frac{dS}{dt}\right)_{\text{irrev}} = \frac{\partial S}{\partial \xi_a}\frac{d\xi_a}{dt} = K_a J_a. \tag{76.3}$$

The rate of the irreversible change of entropy determined by (76.3), always positive, in accordance with the second law of thermodynamics, must be distinguished from the full rate of its change which under a sufficiently intense heat removal from the crystal can sometimes be negative.

The coefficients of the linear dependence of fluxes on forces are called *kinetic coefficients* L_{ac}:

$$J_a = L_{ac}K_c; \tag{76.4}$$

they are connected with coefficients A and C by relations

$$L_{ac} = A_{ab}C_{bc}.$$

Having substituted in (76.3) the values of fluxes J_a expressed with the aid of relation (76.4), we obtain

$$\left(\frac{dS}{dt}\right)_{\text{irrev}} = L_{ab}K_aK_b. \tag{76.5}$$

* As to their meaning, these "forces" do not coincide with "generalized thermodynamic forces" X_a introduced in Ch. VII. This is emphasized by the difference in notation (in manuals on thermodynamics of irreversible processes, mentioned in the preceding footnote, forces conjugate to fluxes are denoted by X).

Since on the strength of the second law of thermodynamics the rate of the irreversible change of entropy is always positive, matrix L is positively definite.

Onsager's reciprocal relations state that matrix L is besides the above symmetric:

$$L_{ac} = L_{ca}. \tag{76.6}$$

However, this formulation of the principle holds only insofar as these coefficients are independent of the magnetic field (or if this field is absent). When the kinetic coefficients depend on the magnetic field $\boldsymbol{H}$, more general relations take place

$$L_{ac}(\boldsymbol{H}) = L_{ca}(-\boldsymbol{H}), \tag{76.7}$$

and relations (76.6) are their concrete expression in case of $\boldsymbol{H} = 0$. Naturally, the positive definiteness as well as relations (76.6) and (76.7) are also equally valid for matrix L^{-1} which specifies the linear dependence of forces on fluxes. Moreover, it is assumed here that quantities $J_a = -\dot{\xi}_a$, called "fluxes", change their sign with time reversal (like all real flows, such as the flow of substance, the flow of heat, electric current). (76.6) and (76.7) also hold if fluxes J_a and J_c are both invariant with respect to time reversal. However, if in case of time reversal only one flux changes its sign, the statements of the Onsager reciprocal relations (76.6) and (76.7) are replaced by the converse ones:

$$L_{ac} = -L_{ca}, \tag{76.6'}$$

$$L_{ac}(\boldsymbol{H}) = -L_{ca}(-\boldsymbol{H}). \tag{76.7'}$$

To show the application of the Onsager reciprocal relations in a concrete situation, we shall consider the process of a simultaneous passage of heat flow and electric current across a crystal. It is defined by an essential non-equilibrium of the crystal—the presence in it of a temperature gradient grad T and a potential gradient grad $\varphi = -\boldsymbol{E}$. Let us denote the density of electric current by $\boldsymbol{j}$ and that of the heat flow by $\boldsymbol{q}$. The density of the total energy flow will then be equal to $\boldsymbol{q} + \varphi\boldsymbol{j}$ where φ is the potential and $\varphi\boldsymbol{j}$ is the energy flow connected with the electric current. Let us calculate the rate of change of entropy

$$\frac{dS}{dt} = \int_V \frac{1}{T}\frac{dU}{dt}\,dV = -\int_V \frac{\operatorname{div}(\boldsymbol{q} + \varphi\boldsymbol{j})}{T}\,dV.$$

Noting that $\operatorname{div}(\boldsymbol{q} + \varphi\boldsymbol{j}) = \operatorname{div}\boldsymbol{q} - \boldsymbol{j}\cdot\boldsymbol{E}$ (note that $\operatorname{div}\boldsymbol{j} = 0$), we write this derivative in the following form

$$\frac{dS}{dt} = -\int_V \frac{\operatorname{div}\boldsymbol{q}}{T}\,dV + \int_V \frac{\boldsymbol{j}\cdot\boldsymbol{E}}{T}\,dV.$$

Let us transform the first integral:

$$-\int_V \frac{\operatorname{div} \boldsymbol{q}}{T}\, dV = -\int_V \operatorname{div}\left(\frac{\boldsymbol{q}}{T}\right) dV + \int_V \boldsymbol{q}\cdot\operatorname{grad}\left(\frac{1}{T}\right) dV =$$

$$= -\oint_\Sigma \frac{\boldsymbol{q}\cdot\boldsymbol{n}}{T}\, d\Sigma - \int_V \frac{\boldsymbol{q}\cdot\operatorname{grad} T}{T^2}\, dV.$$

The surface integral evidently characterizes that part of the rate of change of entropy which is determined by heat supply from the outside; therefore it must be eliminated from $(dS/dt)_{\text{irrev}}$. So, in distinction from dS/dt

$$\left(\frac{dS}{dt}\right)_{\text{irrev}} = \int_V \left(-\frac{\boldsymbol{q}\cdot\operatorname{grad} T}{T^2} + \frac{\boldsymbol{j}\cdot\boldsymbol{E}}{T}\right) dV,$$

or, passing to quantities calculated per unit volume of the crystal

$$\left(\frac{dS}{dt}\right)_{\text{irrev}} = \boldsymbol{q}\cdot\left(-\frac{\operatorname{grad} T}{T^2}\right) + \boldsymbol{j}\cdot\frac{\boldsymbol{E}}{T}. \tag{76.8}$$

It is natural to consider the heat flow $\boldsymbol{q}$ and the current density $\boldsymbol{j}$ as fluxes, then the comparison of (76.8) and (76.3) shows that the forces conjugate to them are respectively the vectors $-(1/T^2)$ grad T and $(1/T)\boldsymbol{E} = -(1/T)$ grad φ.

Relation (76.4) becomes now

$$q_i = L_{il}\left(-\frac{1}{T^2}\frac{\partial T}{\partial x_l}\right) + L_{i(3+m)}\left(\frac{E_m}{T}\right), \tag{76.9}$$

$$j_k = L_{(3+k)l}\left(-\frac{1}{T^2}\frac{\partial T}{\partial x_l}\right) + L_{(3+k)(3+m)}\left(\frac{E_m}{T}\right),$$

and the principle of the symmetry of kinetic coefficients states that matrix L is symmetric, i.e. $L_{ab} = L_{ba}$.

Let us denote

$$\frac{1}{T^2} L_{il} = \lambda^*_{il}, \quad \frac{1}{T} L_{(3+k)(3+m)} = \sigma_{km}, \quad \frac{1}{T^2} L_{(3+k)l} = \beta_{kl};$$

then it follows from the Onsager reciprocal relations that

$$\lambda^*_{il} = \lambda^*_{li}, \quad \sigma_{km} = \sigma_{mk}, \quad \frac{1}{T} L_{i(3+m)} = T\beta_{mi}$$

and equations (76.9) are now expressed as

$$\begin{aligned} q_i &= -\lambda^*_{il}\frac{\partial T}{\partial x_l} + T\beta_{mi}E_m, \\ j_k &= -\beta_{kl}\frac{\partial T}{\partial x_l} + \sigma_{km}E_m. \end{aligned} \tag{76.10}$$

Thus, λ^* is the tensor of the coefficients of thermal conductivity in the absence of an electric field, while $\boldsymbol{\sigma}$ is the tensor of the coeffi-

cients of specific electrical conductivity in the absence of a temperature gradient; their matrices are both positively definite and symmetric. Coefficients β_{kl} characterize the appearance of electric current in the presence of a temperature gradient in the conductor, i.e. a thermoelectric effect. They also characterize the heat flow produced under the action of an electric field even in the absence of a temperature gradient. The internal symmetry of the tensor $\boldsymbol{\beta}$ is V^2.

Besides, the matrix L is positively definite. Hence it follows, in particular, that its diagonal elements are positive, while the squares of the non-diagonal elements are smaller than the products of the corresponding diagonal ones (cf. Sec. 63); for instance,

$$\lambda_{11}^* > 0, \quad \sigma_{33} > 0, \quad \lambda_{12}^{*2} < \lambda_{11}^* \lambda_{22}^*, \quad \sigma_{23}^2 < \sigma_{22}\sigma_{33},$$
$$T\beta_{11}^2 < \lambda_{11}^* \sigma_{11}, \quad T\beta_{12}^2 < \lambda_{22}^* \sigma_{11}.$$

Thermoelectric phenomena in crystals are most often characterized by material equations, equivalent to (76.10), in which, however, independent variables are grad T and $\boldsymbol{j}$:

$$\begin{aligned} E_i &= \rho_{ik} j_k + \alpha_{im} \frac{\partial T}{\partial x_m}, \\ q_l &= T\alpha_{kl} j_k - \lambda_{lm} \frac{\partial T}{\partial x_m}. \end{aligned} \tag{76.11}$$

A simple calculation will show that the coefficients of specific electric resistance ρ_{ik}, coefficients of thermal conductivity in the absence of an electric field λ_{lm}, and thermoelectric coefficients α_{kl} are connected with the earlier introduced coefficients δ_{km}, λ_{il}^* and β_{kl} by the relations

$$\rho_{ik}\sigma_{km} = \delta_{im}, \quad \alpha_{im} = \rho_{ik}\beta_{km}, \quad \lambda_{lm} = \lambda_{lm}^* - T\rho_{ik}\rho_{il}\beta_{km}.$$

The connection between the coefficient of $\partial T/\partial x_n$ in the first of (76.11) equations and the coefficient of j_k in the second equation can also be derived directly from the Onsager reciprocal relations, if we formally accept $\boldsymbol{E}$ and $\boldsymbol{q}$ as "fluxes", so that the "forces" will be $(-1/T^2)$ grad T and $\boldsymbol{j}/T$. However, since $\boldsymbol{q}$ changes its sign with time reversal, and $\boldsymbol{E}$ does not, the formulation of the Onsager reciprocal relations for these coefficients will be (76.6′) and not (76.6); exactly for this reason they have coinciding signs and not opposite ones like the similar coefficients in material equations (76.10).

We shall consider the symmetry of kinetic coefficients, dependent on the magnetic field, in the instance of the thermogalvanomagnetic effect, i.e. kinetic phenomena, developing in a crystal across which heat and electric current are flowing, if the former is placed in a magnetic field*. We shall proceed from a material equation of the type

* On physics of thermogalvanomagnetic phenomena, see, e.g. Vonsovsky (1971).

of (76.11), restricting ourselves to terms linear with respect to the magnetic field (evidently, quadratic terms are similar to those not dependent on the magnetic field, the cubic terms are similar to linear ones and so on):

$$E_i = (L_{ik}^{(0)} + L_{ikn}^{(1)} H_n)\left(\frac{1}{T} j_k\right) + \\ + (L_{i(3+m)}^{(0)} + L_{i(3+m)n}^{(1)} H_n)\left(-\frac{1}{T^2}\frac{\partial T}{\partial x_m}\right), \qquad (76.12)$$

$$q_l = (L_{(3+l)k}^{(0)} + L_{(3+l)kn}^{(1)} H_n)\left(\frac{1}{T} j_k\right) + \\ + (L_{(3+l)(3+m)}^{(0)} + L_{(3+l)(3+m)n}^{(1)} H_n\left(-\frac{1}{T^2}\frac{\partial T}{\partial x_m}\right).$$

Let us apply symmetry relations (76.7′) and connect the coefficients $L_{abn}^{(1)} = (\partial L_{ab}/\partial H_n)_{H=0}$ with thermogalvanomagnetic coefficients:

$$L_{ikn}^{(1)} = -L_{kin}^{(1)} = -T\delta_{ikp} R_{pn},$$
$$L_{(3+l)(3+m)n}^{(1)} = -L_{(3+m)(3+l)n}^{(1)} = T^2 \delta_{lmp} L_{pn},$$
$$L_{i(3+m)n}^{(1)} = L_{(3+m)in}^{(1)} = T^2 N_{imn},$$

then material equations (76.12) will be expressed as

$$E_i = \rho_{ik} j_k + \alpha_{im}\frac{\partial T}{\partial x_m} - \delta_{ikp} R_{pn} H_n j_k - N_{imn} H_n \frac{\partial T}{\partial x_m}, \\ q_l = T\alpha_{kl} j_k - \lambda_{lm}\frac{\partial T}{\partial x_m} + T N_{kln} H_{nk} - j\delta_{lmp} L_{pn} H_n \frac{\partial T}{\partial x_m}. \qquad (76.13)$$

The internal symmetry and the names of tensors of thermogalvanomagnetic effects are as follows:

Tensor	Symmetry	Name
R	V^2	tensor of Hall's coefficients,
L	V^2	tensor of Righi-Leduc coefficients,
N	εV^3	pseudotensor of the Nernst-Ettingshausen coefficients.

They determine the influence of the magnetic field on electric conductivity (Hall's effect), the influence of the magnetic field on thermo-e.m.f. (Nernst effect), the associated influence of the magnetic field on the heat flow caused by the electric current flowing through the conductor (Ettingshausen effect) and, finally, the influence of the magnetic field on thermal conductivity (Righi-Leduc effect). In particular, for isotropic bodies

$$R_{pn} = R\delta_{pn}, \quad L_{pn} = L\delta_{pn}, \quad N_{imn} = N\delta_{imn},$$

so that material equations (76.13) become

$$\begin{aligned} \boldsymbol{E} &= \rho \boldsymbol{j} + \alpha \operatorname{grad} T + R\boldsymbol{H} \times \boldsymbol{j} + N\boldsymbol{H} \times \operatorname{grad} T, \\ \boldsymbol{q} &= T\alpha \boldsymbol{j} - \lambda \operatorname{grad} T + TN\boldsymbol{H} \times \boldsymbol{j} + L\boldsymbol{H} \times \operatorname{grad} T. \end{aligned} \tag{76.14}$$

Thus, in an isotropic body for thermogalvanomagnetic effects, linear with respect to $\boldsymbol{H}$, only that component of the magnetic field is essential which is perpendicular correspondingly to the current or to the temperature gradient, while the changes of the electric field vectors and of the heat flow are in their turn perpendicular to the magnetic field that caused them.

For more details on the thermoelectric and thermogalvanomagnetic effects see Landau and Lifshits (1957); special application of the Onsager reciprocal relations and the thermoelectric phenomena to (non-magnetic) crystals was discussed in great detail by J. F. Nye (1967). Below we shall discuss the generalization of the introduced concepts for magnetic crystals.

It has been noticed recently (Kleiner, 1966) that relations (76.6) and (76.7) can be interpreted as a statement that with time reversal I' the matrix of kinetic coefficients is transposed* and therefore the reciprocal relations in their original treatment are applicable only to non-magnetic substances whose symmetry group contains operation I', while for magnetic crystals a corresponding modification is required. The fact that ordinary formulation (76.6) of the reciprocal relations is inapplicable to magnetic crystals is evident even because the influence of their intrinsic magnetic moment on electrical and thermal conductivity can be interpreted as the Hall and Righi-Leduc spontaneous effects which cause the appearance of antisymmetric components in tensors of electrical resistance and thermal conductivity.

Thus, the processes of electrical and thermal conductivity in crystals of the magnetic class 1 (as well as $\bar{1}$, see below) are described by the equations

$$\begin{aligned} E_i &= \rho_{ik} j_k + \alpha_{im} \frac{\partial T}{\partial x_m}, \\ q_l &= T\gamma_{lkjk} - \lambda_{lm} \frac{\partial T}{\partial x_m}, \end{aligned} \tag{76.15}$$

where $\boldsymbol{\rho}$, $\boldsymbol{\alpha}$, $\boldsymbol{\gamma}$, $\boldsymbol{\lambda}$ are the second-rank tensors, non-symmetric with respect to indices, not interconnected by any relations, except for inequalities following from the positive definiteness of the matrix of kinetic coefficients. As for the Onsager reciprocal relations, it influences the form of these tensors only when some magnetic symmetry is available; this influence is defined by the fact that under the action of rotation R they are transformed into $R\boldsymbol{\rho}$, $R\boldsymbol{\alpha}$, $R\boldsymbol{\gamma}$

* In case when relations (76.6′) and (76.7′) are valid, the matrix of kinetic coefficients is transposed and multiplied by —1.

and $R\lambda$, under the action of time inversion $1'$ matrix L is transposed, and under the action of operation $R' = 1'R$ these two transformations occur together. In this case for all operations g contained in the point group of the crystal's magnetic symmetry, $gL = L$. In particular, for operations of the type $R' = 1'R$, characterized by rotation matrix $\|r_{i'k}\|$, this condition means that the components of tensors $\boldsymbol{\rho}$ and $\boldsymbol{\lambda}$ satisfy the equalities

$$(r_{i'l}r_{j'k} - \delta_{i'k}\delta_{j'l})\rho_{kl} = 0, \tag{76.16}$$

and the components of tensors $\boldsymbol{\alpha}$ and $\boldsymbol{\gamma}$ satisfy the equalities

$$r_{i'l}r_{j'k}\alpha_{kl} = \delta_{i'k}\delta_{j'l}\gamma_{kl}. \tag{76.17}$$

Moreover, it should be borne in mind that tensors $\boldsymbol{\rho}$, $\boldsymbol{\lambda}$, $\boldsymbol{\alpha}$, $\boldsymbol{\gamma}$ (as well as the pseudotensors describing thermogalvanomagnetic effects) are centrosymmetric and therefore are the same for all magnetic groups contained in one Laue class, i.e. combined in one square of column G_1 of Table 72.4. The Laue classes for magnetic groups are divided into three types, as can be seen from the Table: white, black-white and grey ones. The white Laue classes contain only white groups, and for that matter all of them. The grey Laue classes contain, along with the grey groups $G1'$ also black-white groups $G\bar{1}'$ which have among their elements the centre of antisymmetry $\bar{1}'$. Finally, the black-white Laue classes contain only black-white groups, namely, just those which do not possess element $\bar{1}'$.

On the basis of these considerations we obtain for the grey Laue classes, i.e. for groups $G1'$ and $G\bar{1}'$, the classical formulation of the Onsager reciprocal relations: $\rho_{ik} = \rho_{ki}$, $\lambda_{ik} = \lambda_{ki}$, $\gamma_{ik} = \alpha_{ki}$, and all these tensors are invariant with respect to G. For white groups G tensors $\boldsymbol{\rho}$, $\boldsymbol{\lambda}$, $\boldsymbol{\alpha}$, $\boldsymbol{\gamma}$ are invariant with respect to G, but generally speaking, they are non-symmetric with respect to indices and are in no way interconnected. For the black-white Laue classes special rules tabulated in Table 76.1 are derived with the aid of (76.16) and (76.17).

Thermogalvanomagnetic coefficients, i.e. third-rank pseudotensors, which define increments to the principal coefficients linear with respect to $\boldsymbol{H}$ are derived similarly (see Kleiner, 1969). In case of a complete absence of symmetry

$$E_i = \rho_{ik}j_k + \alpha_{im}\frac{\partial T}{\partial x_m} - P_{ikn}H_n j_k - N_{imn}H_n\frac{\partial T}{\partial x_m},$$

$$q_l = T\gamma_{lk}j_k - \lambda_{lm}\frac{\partial T}{\partial x_m} - TM_{lkn}H_n j_k - Q_{lmn}H_n\frac{\partial T}{\partial x_m}. \tag{76.18}$$

Thus, in this case matrix $(\partial L/\partial H)_0$ is determined by four third-rank pseudotensors, **P**, **Q**, **N**, **M** which are not interconnected entirely and have no internal symmetry. Since time inversion $1'$ not only transposes matrix $(\partial L/\partial \mathbf{H})_0$, but also reverses its sign, the presence of

Table 76.1

Kinetic Coefficients of the Process of Electrical and Thermal Conductivity in Magnetic Crystals of the Black-White Laue Classes

$2'/m'$	ρ_{11}	ρ_{12}	ρ_{13}	α_{11}	α_{12}	α_{13}
	ρ_{12}	ρ_{22}	ρ_{23}	α_{21}	α_{22}	α_{23}
	$-\rho_{13}$	$-\rho_{23}$	ρ_{33}	α_{31}	α_{32}	α_{33}
	α_{11}	α_{21}	$-\alpha_{31}$	λ_{11}	λ_{12}	λ_{13}
	α_{12}	α_{22}	$-\alpha_{32}$	λ_{12}	λ_{22}	λ_{23}
	$-\alpha_{13}$	$-\alpha_{23}$	α_{33}	$-\lambda_{13}$	$-\lambda_{23}$	λ_{33}
$mm'm'$	ρ_{11}	ρ_{12}	0	α_{11}	α_{12}	0
	$-\rho_{12}$	ρ_{22}	0	α_{21}	α_{22}	0
	0	0	ρ_{33}	0	0	α_{33}
	α_{11}	$-\alpha_{21}$	0	λ_{11}	λ_{12}	0
	$-\alpha_{12}$	α_{22}	0	$-\lambda_{12}$	λ_{22}	0
	0	0	α_{33}	0	0	λ_{33}
∞/mm' $6/mm'm$ $4/mm'm'$ $\bar{3}m'$	ρ_{11}	ρ_{12}	0	α_{11}	α_{12}	0
	$-\rho_{12}$	ρ_{11}	0	$-\alpha_{12}$	α_{11}	0
	0	0	ρ_{33}	0	0	α_{33}
	α_{11}	α_{12}	0	λ_{11}	λ_{12}	0
	$-\alpha_{12}$	α_{11}	0	$-\lambda_{12}$	λ_{11}	0
	0	0	α_{33}	0	0	λ_{33}
$4'/m$	ρ_{11}	0	0	α_{11}	α_{12}	0
	0	ρ_{11}	0	α_{21}	α_{22}	0
	0	0	ρ_{33}	0	0	α_{33}
	α_{22}	$-\alpha_{12}$	0	λ_{11}	0	0
	$-\alpha_{21}$	α_{11}	0	0	λ_{11}	0
	0	0	α_{33}	0	0	λ_{33}
$4'/mmm'$	ρ_{11}	0	0	α_{11}	0	0
	0	ρ_{11}	0	0	α_{22}	0
	0	0	ρ_{33}	0	0	α_{33}
	α_{22}	0	0	λ_{11}	0	0
	0	α_{11}	0	0	λ_{11}	0
	0	0	α_{33}	0	0	λ_{33}
$6'/m'$	ρ_{11}	0	0	α_{11}	α_{12}	0
	0	ρ_{11}	0	$-\alpha_{12}$	α_{11}	0
	0	0	ρ_{33}	0	0	α_{33}
	α_{11}	$-\alpha_{12}$	0	λ_{11}	0	0
	α_{12}	α_{11}	0	0	λ_{11}	0
	0	0	α_{33}	0	0	λ_{33}
$6'/m'mm$	ρ_{11}	0	0	α_{11}	0	0
	0	ρ_{11}	0	0	α_{11}	0
	0	0	ρ_{33}	0	0	α_{33}
	α_{11}	0	0	λ_{11}	0	0
	0	α_{11}	0	0	λ_{11}	0
	0	0	α_{33}	0	0	λ_{33}
$m3m'$	ρ_{11}	0	0	α_{11}	0	0
	0	ρ_{11}	0	0	α_{11}	0
	0	0	ρ_{11}	0	0	α_{11}
	α_{11}	0	0	λ_{11}	0	0
	0	α_{11}	0	0	λ_{11}	0
	0	0	α_{11}	0	0	λ_{11}

operation $R' = 1'R$ in the crystal's magnetic symmetry group involves relations similar to (76.16) for tensors **P** and **Q**:

$$(r_{i'm}r_{j'l}r_{k'n} + \delta_{i'l}\delta_{j'm}\delta_{k'n})\, P_{lmn} = 0 \qquad (76.19)$$

and relations similar to (76.17) for tensors **M** and **N**:

$$-r_{i'm}r_{j'l}r_{k'n}N_{lmn} = \delta_{i'l}\delta_{j'm}\delta_{k'n}M_{lmn}. \qquad (76.20)$$

By their means it is possible to find the form of matrices $(\partial L/\partial H)_0$ and of pseudotensors contained in equations (76.18) for all black-white Laue classes.

Hall's coefficients are apparently the most interesting of the thermogalvanomagnetic coefficients. While in non-magnetic crystals Hall's effect is specified by the second-rank (generally speaking, non-symmetric) tensor **R**, in magnetic crystals is required for this purpose a non-symmetric third-rank pseudotensor **P**. This pseudotensor can conveniently be expanded however, into antisymmetric part and a part symmetric with respect to the first two indices. It is possible to represent the former part with the aid of a second-rank tensor, so that

$$P_{ikn} = \delta_{ikp} R_{pn} + S_{ikn},$$

$$S_{ikn} = \frac{1}{2}(P_{ikn} + P_{kin}), \quad R_{pn} = \frac{1}{2}\delta_{pik} P_{ikn}.$$

Each of these parts for any class G of magnetic symmetry can easily be determined with the aid of Tables. The antisymmetric part is obviously invariant not only with respect to the senior group $G\bar{1}$ of the Laue class to which G belongs, but also with respect to group $G\bar{1}1'$. From the Table E.6 we shall find for it the form of tensor R by means of which we can also easily restore $\delta_{ikp}R_{pn}$. Finding the form of the symmetric part calls for the determination of the piezomagnetic tensor for the given Laue class $G\bar{1}$ (a simple method is explained in Sec. 73); thereupon the indices should be rearranged so that those with which the tensor is symmetric are placed in front.

The terms quadratic in **H** in the dependence of specific electrical resistance on the magnetic field, are introduced by a fourth-rank tensor **T**, so that

$$E_i = (\rho_{ik} + P_{ikm}H_m + T_{ikmn}H_m H_n)\, j_k.$$

Tensor **T** is called the *tensor of magnetic resistance.* Apparently it is always symmetric with respect to the last two indices:

$$T_{ikmn} = T_{iknm}. \tag{76.21}$$

Besides, it is symmetric with respect to the first two indices in all grey Laue classes ($T_{ikmn} = T_{kimn}$), so that its form can be found from Table E.19. In the white Laue classes tensor **T** is generally non-symmetric with respect to the first two indices, therefore its form should be determined with the aid of Table E.21. Finally, the form of the tensor of magnetic resistance in the black-white Laue classes is determined by the fact that if operation $R' = 1'R$ is contained in the magnetic symmetry group of the crystal,

$$(r_{i'n}r_{j'm}r_{k'p}r_{l'q} - \delta_{i'm}\delta_{j'n}\delta_{k'p}\delta_{l'q})\, T_{mnpq} = 0 \tag{76.22}$$

this being an analogue of relations (76.16) and (76.19). The form of the tensor of magnetic resistance for all 10 crystallographic black-white Laue classes that follows from relations (76.21) and (76.22) is given by Pantulu and Sudarshan (1970).

Sec. 77. Electrooptical and Piezooptical Effects

The changes of the optical properties of crystals under the influence of an electric field and mechanical stresses were noticed back in the 19th century and are widely used in practice. Under the influence of electric field $\boldsymbol{E}$ and mechanical stresses $\boldsymbol{\sigma}$ the tensor of dielectric impermeability of a crystal $\boldsymbol{\eta} = \boldsymbol{\eta}(\omega)$ slightly changes becoming equal to $\boldsymbol{\eta} + \boldsymbol{\zeta}$ where the symmetric second-rank tensor $\boldsymbol{\zeta} = \boldsymbol{\zeta}(\mathbf{E}, \boldsymbol{\sigma})$ is a small increment to the tensor of dielectric impermeability (cf. Sec. 20). Since the optical indicatrix $\eta_{ij}\, x_i x_j = 1$ is the representation surface of the tensor of dielectric impermeability $\boldsymbol{\eta}$, the studied effects can be lucidly imagined as the result of the strain of the crystal's optical indicatrix under the influence of the electric field and mechanical stresses.

The change of the dielectric impermeability of a substance at optical frequencies under the action of mechanical stresses is called the *piezooptical effect* or *photoelasticity**. Sufficient accuracy for crystals is already given by the first (linear) approximation

$$\boldsymbol{\zeta} = \boldsymbol{\pi} : \boldsymbol{\sigma}, \quad \zeta_{ij} = \pi_{ijkl}\sigma_{kl}. \tag{77.1}$$

The fourth-rank tensor $\boldsymbol{\pi}$ is called the *tensor of the piezooptical coefficients.* Due to the symmetry of tensor $\boldsymbol{\zeta}$ it is symmetric with respect to the first pair of indices, and due to the symmetry of $\boldsymbol{\sigma}$ also with respect to the second pair. Thus

$$\pi_{ijkl} = \pi_{jikl} = \pi_{ijlk} = \pi_{jilk}, \tag{77.2}$$

i.e. its internal symmetry is $[V^2]^2$. The piezooptical effect can occur in media of any symmetry, including isotropic bodies.

The general form of the tensor of piezooptical coefficients in the crystal-physical system of coordinates for the crystals of all classes is given in Table E.19, the components $\pi_{\lambda\mu}$ corresponding to the notation of the piezooptical effect as

$$\zeta_\lambda = \pi_{\lambda\mu}\sigma_\mu. \tag{77.3}$$

Here it is conventionally considered that

$$\begin{aligned} \zeta_\lambda &= \zeta_{ij} \quad (ij \leftrightarrow \lambda = 1, \ldots, 6), \\ \sigma_\mu &= \sigma_{kl} \quad (kl \leftrightarrow \mu = 1, \ldots, 6). \end{aligned} \tag{77.4}$$

Hence we obtain (see Appendix F) the rules for recalculation

$$\pi_{\lambda\mu} = \begin{cases} \pi_{ijkl} & (ij \leftrightarrow \lambda = 1, \ldots, 6; \quad kl \leftrightarrow \mu = 1, 2, 3), \\ 2\pi_{ijkl} & (ij \leftrightarrow \lambda = 1, \ldots, 6; \quad kl \leftrightarrow \mu = 4, 5, 6). \end{cases} \tag{77.5}$$

* The piezooptical effect was discovered by Brewster — first in isotropic transparent bodies, and later in crystals (1818).

The change of the tensor of dielectric impermeability can also be expressed by strains:

$$\boldsymbol{\zeta} = \mathbf{p} : \boldsymbol{\varepsilon}, \quad \zeta_{ij} = p_{ijkl}\varepsilon_{kl}. \tag{77.6}$$

Tensor **p** is called the *tensor of elastooptical coefficients.* Its internal symmetry coincides with the internal symmetry of tensor $\boldsymbol{\pi}$. The contracted notation of (77.6) is

$$\zeta_\lambda = p_{\lambda\mu}\varepsilon_\mu. \tag{77.7}$$

On the basis of the recalculation rules for ζ_λ (77.4) and for ε_μ (F.4), we obtain

$$p_{\lambda\mu} = p_{ijkl} \quad (ij \leftrightarrow \lambda = 1, \ldots, 6; \quad kl \leftrightarrow \mu = 1, \ldots, 6) \tag{77.8}$$

The general form of the tensor of piezooptical coefficients in the crystal-physical reference frame for crystals of all classes is given in Table E.19; some distinctions between the relations connecting the coefficients $\pi_{\lambda\mu}$ and $p_{\lambda\mu}$ are explained by the difference between the rules for recalculation (77.5) and (77.8).

Insofar as the elastic strains and stresses are interrelated by Hooke's law $\boldsymbol{\varepsilon} = \mathbf{s} : \boldsymbol{\sigma}$, $\boldsymbol{\sigma} = \mathbf{c} : \boldsymbol{\varepsilon}$, the relation between the piezooptical and elastooptical coefficients can be easily established:

$$p_{\lambda\mu} = \pi_{\lambda\nu}c_{\nu\mu}, \quad \pi_{\lambda\mu} = p_{\lambda\nu}s_{\nu\mu}. \tag{77.9}$$

The situation becomes more complicated when a crystal experiences not only elastic but also plastic strains. Studying plastically strained monocrystals of silver chloride, Markovsky, Polukhin and Shaskolskaya (1966) showed that for this material considered in the plastic region—up to deformations of about 20%—there exists a linear dependence of the change of the tensor of dielectric impermeability $\boldsymbol{\eta}$ on the stress tensor $\boldsymbol{\sigma}$ expressed by formulas (77.1) and (77.3) and with the same coefficients, while formulas (77.6) and (77.7) are inapplicable: the change of the optical indicatrix is determined not by full strain $\boldsymbol{\varepsilon}$, but only by its elastic part $\boldsymbol{\varepsilon}_{\text{elast}} = \mathbf{s} : \boldsymbol{\sigma}$.

The tensor of the elastooptical coefficients **p** plays an important role in the Mandel'shtam-Brillouin effect, i.e. in scattering light on thermal elastic vibrations of a crystal*. Straining the crystal the elastic (supersonic) wave with a displacement $\boldsymbol{u} = A\boldsymbol{p} \exp[(2\pi i/\lambda)(\boldsymbol{m}\cdot\boldsymbol{r} - vt)]$ (see Sec. 56) causes changes of the optical indicatrix $\zeta_{ij}(\boldsymbol{\varepsilon}) = p_{ijkl}\varepsilon_{kl}$ where the tensor of small strains $\varepsilon_{kl} = \frac{1}{2}(\partial u_k/\partial x_l + \partial u_l/\partial x_k)$. Due to the symmetry of the tensor of elastooptical coefficients p_{ijkl} with respect to the last two indices, $\zeta_{ij}(\boldsymbol{\varepsilon})$ can also be represent-

* The scattering of light in crystals is discussed in a monograph by Fabelinsky (1965).

ed as

$$\zeta_{ij}(\varepsilon) = p_{ijkl}\frac{\partial u_k}{\partial x_l}. \tag{77.10}$$

The Mandel'shtam-Brillouin scattering represents in essence the diffraction of light on a periodic structure $\zeta_{ij} = Z_{ij}\exp[(2\pi i/\lambda)(\boldsymbol{m}\cdot\boldsymbol{r} - vt)]$, accompanied by the Doppler effect caused by the motion of this structure with a supersonic velocity v. It was noticed recently (Nelson, Lax, 1970) that rotations of the crystal volume elements as a whole, caused by an elastic wave

$$\omega_{kl} = (A\pi i/\lambda)(p_k m_l - m_k p_l)\exp[(2\pi i/\lambda)(\boldsymbol{m}\cdot\boldsymbol{r} - vt)]$$

at a not too small birefringence of the crystal make a perceptible contribution to the Mandel'shtam-Brillouin scattering. Indeed, at such rotations the optical indicatrix of the volume element rotates together with it. The coefficients of the optical indicatrix thus rotated with respect to the stationary, i.e. to the connected with the whole crystal, coordinate system are equal to $\eta^*_{ij} = c_{k'i}c_{l'j}\eta_{k'l'}$, where $\eta_{k'l'}$ are the coefficients of the optical indicatrix referred to the rotated system, while $c_{k'i}$ are the elements of the transformation matrix. Since, according to (17.7), at a small angle of rotation $c_{k'i} = \delta_{k'i} + \delta_{k'ij}\varphi_j$, and the tensor of small rotations is connected with the angle of rotation by the relation $\omega_{ki} = -\delta_{kij}\varphi_j$ that directly follows from (49.6), the sought-for coefficients of the rotated optical indicatrix are equal to

$$\eta^*_{ij} = (\delta_{ki} - \omega_{ki})(\delta_{lj} - \omega_{lj})\eta_{kl}. \tag{77.11}$$

The accented summation indices are replaced here by unaccented ones; naturally this does not change the sum but is more convenient for interpretation: η_{kl} are conceived here as the coefficients of the optical indicatrix of the crystal in the absence of external influences, referred to the stationary reference frame. The changes of the components of the dielectric impermeability tensor, caused by the rotation, are equal to $\zeta_{ij}(\boldsymbol{\omega}) = \eta^*_{ij} - n_{ij}$. Substituting the value of η^*_{ij} from (77.11) and neglecting the terms quadratic with respect to $\boldsymbol{\omega}$, we obtain $\zeta_{il}(\boldsymbol{\omega}) = -\eta_{il}\omega_{lj} - \eta_{kj}\omega_{ki}$. Taking into account the antisymmetry of tensor $\boldsymbol{\omega}$ this result can be represented in the form

$$\zeta_{ij}(\boldsymbol{\omega}) = (\eta_{il}\delta_{jk} - \eta_{kj}\delta_{il})\,\omega_{kl}.$$

Let us antisymmetrize tensor $\eta_{il}\delta_{jk} - \eta_{kj}\delta_{il}$ with respect to indices k and l. Denoting the result of antisymmetrization by $q_{ij[kl]}$, we obtain

$$q_{ij[kl]} = \frac{1}{2}(\eta_{il}\delta_{jk} - \eta_{kj}\delta_{il} + \eta_{lj}\delta_{ik} - \eta_{ik}\delta_{lj}). \tag{77.12}$$

When multiplied by ω_{kl} tensor $q_{ij[kl]}$ gives the same result as $\eta_{il}\delta_{jk} - \eta_{kj}\delta_{il}$, but $q_{ij[kl]}\varepsilon_{kl} = 0$, therefore $\zeta_{ij}(\boldsymbol{\omega})$ can be calculated from the distortion $\partial\boldsymbol{u}/\partial\boldsymbol{r}$:

$$\zeta_{ij}(\boldsymbol{\omega}) = q_{ij[kl]}\frac{\partial u_k}{\partial x_l}. \tag{77.13}$$

Comparing (77.10) and (77.13) we see that it is possible to form a generalized tensor of elastooptical coefficients non-symmetric with respect to the last two indices

$$q_{ijkl} = p_{ijkl} + q_{ij[kl]} \tag{77.14}$$

(the ordinary tensor of elastooptical coefficients $\mathbf{p}$ is in this case its symmetric part: $p_{ijkl} = q_{ij[kl]}$ and to represent with its aid the complete changes of the

optical indicatrix coefficients $\zeta = \zeta(\varepsilon) + \zeta(\omega)$ as

$$\zeta_{ij} = q_{ijkl}\frac{\partial u_k}{\partial x_l}, \quad \zeta = \mathbf{q} : \frac{\partial \mathbf{u}}{\partial \mathbf{r}}. \tag{77.15}$$

Let us note that tensor $q_{ij[kl]}$ is determined not even by the whole tensor η, but only by its deviator, therefore tensor $\mathbf{q}$ in a general case has not $6 \cdot 9 = 54$ independent components as a tensor with internal symmetry $[V^2]$ V^2 should have, but only 41, i.e. by five more than tensor $\mathbf{p}$ with internal symmetry $[V^2]^2$.

Let us now consider the influence of an electric field on a crystal's optical indicatrix. We shall begin with the *linear electrooptical effect* which is also called the *Pockels effect* (Pockels, 1894). It is described by the formula

$$\zeta = \mathbf{r} \cdot E, \quad \zeta_{ij} = r_{ijk}E_k. \tag{77.16}$$

The third-rank tensor $\mathbf{r}$ is called the *tensor of electrooptical coefficients.* Due to the symmetry of tensor ζ the internal symmetry of tensor $\mathbf{r}$ is the same as that of the tensor of piezoelectric coefficients $\mathbf{d}$. Hence it is clear that the linear electrooptical effect is possible only in those crystals whose symmetry permits the presence of piezoelectric properties (see Sec. 58). A contracted notation of (77.16) is as follows:

$$\zeta_\lambda = r_{\lambda k}E_k; \tag{77.17}$$

in accordance with (77.4) the recalculation rule is

$$r_{\lambda k} = r_{ijk} \ (ij \leftrightarrow \lambda = 1, \ldots, 6). \tag{77.18}$$

The general form of tensor $\mathbf{r}$ for all crystallographic classes is given in Table E.11.

The electrooptical coefficients depend, generally speaking, on the conditions under which they are measured. Two cases are of practical importance: (1) mechanical stresses are zero (the crystal is mechanically free and can be strained due to converse piezoelectric effect)—we shall denote the corresponding electrooptical coefficients by $\mathbf{r}^{(\sigma)}$; (2) the crystal cannot be strained (it is mechanically clamped)—the correspoding coefficients are $\mathbf{r}^{(\varepsilon)}$. To calculate the difference $\mathbf{r}^{(\sigma)} - \mathbf{r}^{(\varepsilon)}$ let us consider the simultaneous action of the electrooptical and piezooptical effects, as well as strains developing in a crystal under the influence of an electric field and the field of mechanical stresses:

$$\begin{aligned} \zeta_\lambda &= r_{\lambda k}E_k + \pi_{\lambda\mu}\sigma_\mu, \\ \varepsilon_\varkappa &= d_{k\varkappa}E_k + s_{\varkappa\mu}\sigma_\mu. \end{aligned} \tag{77.19}$$

Here $\mathbf{d}$ and $\mathbf{s}$ are the tensors of piezoelectric and elastic compliance coefficients. When the crystal is mechanically clamped, $\varepsilon = 0$, so that $\sigma_\mu = -c_{\mu\varkappa}d_{k\varkappa}E_k$. Therefore in a mechanically clamped crystal the electrooptical increment to the tensor of dielectric impermeabil-

ity is equal to

$$\zeta_\lambda = (r_{\lambda k}^{(\sigma)} - d_{k\varkappa} c_{\varkappa\mu} \pi_{\lambda\mu}) E_k. \tag{77.20}$$

Apparently exactly the expressions in brackets are the electrooptical coefficients of a mechanically clamped crystal. Using (77.9) the relation between electrooptical coefficients of a free and a mechanically clamped crystal can be represented as

$$r_{\lambda k}^{(\sigma)} - r_{\lambda k}^{(\varepsilon)} = d_{k\varkappa} p_{\lambda\varkappa}. \tag{77.21}$$

As was already noted, the linear electrooptical effect is possible only in crystals relating to piezoelectric symmetry classes. But artificial birefringence under the action of an electric field can be observed also in such substances whose symmetry is known to eliminate any possibility of the piezoelectric effect, for instance, in isotropic substances—in liquids and even in gases. In all these cases, however, the effect is proportional not to the electric field intensity but to its square, and does not alter under a reversal of the direction of the electric field. This is the *quadratic electrooptical effect*, or the *Kerr effect.*

The increment to the tensor of dielectric impermeability caused by the quadratic electrooptical effect has the following form

$$\zeta_{ij} = K_{ijkl} E_k E_l, \ \zeta\lambda + K_{\lambda\mu} (EE)_\mu, \tag{77.22}$$

where the recalculation rules for ζ_λ are definded by (77.4), and for $(EE)_\mu$, by the formula

$$(EE)_\mu = E_k E_l \quad (kl \leftrightarrow \mu = 1, \ldots, 6). \tag{77.23}$$

The fourth-rank tensor K is called the *tensor of Kerr's coefficients*; its internal symmetry is the same as that of the tensor of piezooptical coefficients π; moreover, the recalculation rules for these tensors also coincide:

$$K_{\lambda\mu} = \begin{cases} K_{ijkl} & (ij \leftrightarrow \lambda = 1, \ldots, 6; \quad kl \leftrightarrow \mu = 1, 2, 3), \\ 2K_{ijkl} & (ij \leftrightarrow \lambda = 1, \ldots, 6, \quad kl \leftrightarrow \mu = 4, 5, 6) \end{cases} \tag{77.24}$$

(cf. (77.5)). Therefore the general form of the tensor of Kerr's coefficients in the crystal-physical system of coordinates for crystals of all classes is given by the same Table E.19 that gives the general form of the tensor of piezooptical coefficients.

The quadratic electrooptical effect can be observed also in crystals that manifest linear electrooptical effect. In the majority of cases it causes only small increments to the principal linear effect, but if the electric field in the experiment has the direction which does not cause the development of the linear electrooptical effect, the determining role is played by the quadratic electrooptical effect.

Sec. 78. Artificial Optical Anisotropy of Crystals

Artificially Uniaxial and Biaxial Crystals. Optically isotropic media—crystals of the cubic system and isotropic bodies—can remain optically isotropic under the action of external agents or can become like uniaxial or biaxial crystals, which will immediately be seen in the conoscopic picture (see Sec. 40). The first case occurs under the action of uniform pressure p, the tensor ζ being isotropic. When the external action transforms an optically isotropic medium into one resembling a uniaxial crystal, the symmetry of tensor ζ is ∞/mm; for this to happen the strained medium must retain a three-fold or a higher-order symmetry axis. This means that to impart optical anisotropy peculiar to a uniaxial crystal to an isotropic medium it will suffice to subject this medium to the action of an arbitrarily directed electric field or of uniaxial extension. In a crystal of the higher subsytem of the cubic system electric field or uniaxial extension should be directed along one of the three- or four-fold axes, i.e. in the direction ⟨111⟩ or ⟨100⟩ and in the crystals of the lower subsystem of the cubic system—along the three-fold axis ⟨111⟩.

In their action on an isotropic body mechanical stresses, not reducing to hydrostatic pressure and uniaxial stress, liken it to a biaxial crystal with respect to its optical properties. The same result is produced on the crystals of the cubic system by the action of uniaxial extension or an electric field not directed along a three- or four-fold axis.

Let us consider, for example, the change of optical properties of a crystal of the lower subsystem of the cubic system under the action of uniaxial extension with intensity σ and directed along [001], in such crystals it is a two-fold axis. The increment to the tensor of dielectric impermeability is equal to

$$\zeta = \pi\colon \sigma e_3 e_3 = (\pi_{21} e_1 e_1 + \pi_{12} e_2 e_2 + \pi_{11} e_3 e_3)\,\sigma, \tag{78.1}$$

where e_1, e_2, e_3 are the mutually orthogonal unit vectors of the crystal-physical system of coordinates. The principal axes of the thus changed tensor of dielectrit impermeability coincide with these unit vectors. For further investigation ie would be convenient to find out which of the principal refractive indices is the largest and which is the smallest one. Thus, in potassium alum, barium nitrate and lead nitrate $\pi_{11} < \pi_{21} < \pi_{12}$, therefore

$$\begin{aligned} N_g^{-2} &= N_3^{-2} = n_0^{-2} + \pi_{11}\sigma, \\ N_m^{-2} &= N_1^{-2} = n_0^{-2} + \pi_{21}\sigma, \\ N_p^{-2} &= N_2^{-2} = n_0^{-2} + \pi_{12}\sigma. \end{aligned} \tag{78.2}$$

Thus, the optic axes of a stressed crystal lie in the plane (100) and each of them makes up an angle V with axis [001] which is determined from the relation

$$\tan V = \sqrt{\frac{N_p^{-2} - N_m^{-2}}{N_m^{-2} - N_g^{-2}}}$$

(see Sec. 35). Substituting into this formula the inverse squares of the principal refractive indices, we find

$$\tan V = \sqrt{\frac{\pi_{12} - \pi_{21}}{\pi_{21} - \pi_{11}}}. \tag{78.3}$$

Although the principal refractive indices do depend on the intensity of influence, the angle between the optic axes does not; it is determined only by the character and direction of the influence and by the piezooptical (or correspondingly electro-optical) properties of the crystal.

Uniaxial crystals will remain uniaxial under the action of an electric field directed along the principal symmetry axis, as well as under the action of uniaxial stress of the same direction, and hydrostatic compression. All other influences will liken these crystals to biaxial ones.

For assessing the artificial biaxiality let us calculate half of the angle between the optic axes of a stressed crystal. Let us use for this purpose the results obtained in Sec. 20. That is, we shall consider that the small (in comparison with η) tensor ζ is referred to the crystal-physical system of coordinates. Let us denote the eigenvalues of a two-dimensional tensor

$$\begin{Vmatrix} \zeta_{11} & \zeta_{12} \\ \zeta_{12} & \zeta_{22} \end{Vmatrix}$$

by $\xi_{(1)}$ and $\xi_{(2)}$ ($\xi_{(1)} > \xi_{(2)}$). Assuming for definiteness that an unstressed crystal is optically positive, we have

$$\begin{aligned} N_g^{-2} &= N_e^{-2} + \zeta_{33}, \\ N_m^{-2} &= N_o^{-2} + \xi_{(2)}, \\ N_p^{-2} &= N_o^{-2} + \xi_{(1)}. \end{aligned} \tag{78.4}$$

Then half of the angle between the optic axes

$$V \approx \tan V = \sqrt{\frac{\xi_{(1)} - \xi_{(2)}}{N_o^{-2} - N_e^{-2}}}. \tag{78.5}$$

Thus the crystal remains positive ($V \ll 45°$) also under an influence. Substituting into (78.5) the value of the difference $\xi_{(1)} - \xi_{(2)}$, we obtain

$$\tan V = \frac{\sqrt[4]{(\zeta_{11} - \zeta_{22})^2 + (2\zeta_{12})^2}}{\sqrt{N_0^{-2} - N_e^{-2}}}. \tag{78.6}$$

If the artificial biaxiality is caused by the piezooptical effect, then

$$\tan V = \frac{\sqrt[4]{[(\pi_{1\mu} - \pi_{2\mu})\,\sigma_\mu]^2 + (2\pi_{6\mu}\sigma_\mu)^2}}{\sqrt{N_o^{-2} - N_e^{-2}}}, \tag{78.7}$$

and if by the electrooptical effect, then

$$\tan V = \frac{\sqrt[4]{[(r_{1k} - r_{2k})\, q_k]^2 + (2r_{6k} q_k)^2}}{\sqrt{N_o^{-2} - N_e^{-2}}} \sqrt{E}, \qquad (78.8)$$

where $E = Eq$ is the intensity of the electric field. Formulas for negative crystals are derived similarly.

Let us note characteristic distinctions of artificial birefringence in uniaxial and optically isotropic crystals. In uniaxial crystals the angle between optic axes is small and depends on the intensity of the exerted influence; thus, in case of the piezooptical effect it is proportional to $\sqrt{\sigma}$, in case of the electrooptical effect, to $\sqrt{E}$, in case of the Kerr effect, to $|E|$. In optically isotropic crystals this angle is not generally small and does not depend on the influence intensity. When the influence on the cubic crystal is gradually diminished, the exits of the optic axes in the conoscopic pictures are not displaced, but all the isochromes are gradually broadened and disappear from the field of vision. On the contrary, when the influence on uniaxial crystals is diminished, the exits of the optic axes in the conoscopic picture begin drawing together, at first slowly, then increasing quicker, until their full coincidence, while the number of isochromes forming the conoscopic picture remains practically unchanged, since in this case it is determined by the natural birefringence of the crystal. Thus, in case of the artificial birefringence, the angle between the optic axes characterizes the intensity of external influence only in uniaxial crystals.

Internal stresses developing in crystals during their growth result, in particular, in artificial birefringence.

Artificial Birefringence. Artificial birefringence is the name of the change of birefringence of crystals under external influences, such as mechanical stresses or electric fields, in particular, the appearance of birefringence in those crystals or in those directions where there was none in the absence of influence.

Let the direction of light propagation be such that in the absence of an electric field or mechanical stresses there is also no birefringence (in crystals of the lower and intermediate categories it is the direction of the optic axes, and in crystals of the higher category and in isotropic bodies, any direction). Under the action of an electric field or mechanical stresses there appears artificial birefringence in this direction. Let us calculate its magnitude, bearing in mind that the increment, ζ, to the dielectric impermeability tensor η is small.

Let us introduce a special Cartesian coordinate system X_1', X_2', X_3', directing axis X_3' along the wave normal; then axes X_1' and X_2' will lie in the plane of the wave front. The central section of the optical indicatrix, undisturbed by the plane of the wave front, is described

in the special coordinate system by the equations

$$\eta'_{\alpha\beta}x'_\alpha x'_\beta = 1 \quad (\alpha,\ \beta = 1,\ 2), \quad x'_3 = 0. \tag{78.9}$$

This is a circumference of radius n_o, where n_o is the index of the refraction of light propagating along the optic axis in a free crystal. Indeed, axis X'_3 coincides with the optic axis and therefore

$$\eta'_{11} = \eta'_{22} = n_o^{-2}, \quad \eta'_{12} = 0, \tag{78.10}$$

so that the first of the equations (78.9) comes to $n_o^{-2}\,[(x'_1)^2 + (x'_2)^2] = 1$.

A disturbed optical indicatrix is described by an equation

$$\boldsymbol{r}\cdot(\eta + \zeta)\cdot\boldsymbol{r} = 1, \quad (\eta_{ij} + \zeta_{ij})x_i x_j = 1, \tag{78.11}$$

and its central section by the plane of the wave front, by equations

$$(\eta'_{\alpha\beta} + \zeta'_{\alpha\beta})\,x'_\alpha x'_\beta = 1 \quad (\alpha,\ \beta = 1,\ 2), \quad x'_3 = 0. \tag{78.12}$$

Taking account of equalities (78.10), we rewrite equation (78.12) in the form

$$(n_o^{-2} + \zeta'_{11})\,(x'_1)^2 + (n_o^{-2} + \zeta'_{22})\,(x'_2)^2 + 2\zeta'_{12}x'_1x'_2 = 1.$$

The refractive indices n_1 and n_2 of linearly polarized waves passing across a stressed crystal are defined by means of a quadratic equation in n^{-2}

$$\begin{vmatrix} n_o^{-2} + \zeta'_{11} - n^{-2} & \zeta'_{12} \\ \zeta'_{12} & n_o^{-2} + \zeta'_{22} - n^{-2} \end{vmatrix} = 0. \tag{78.13}$$

Having solved it, we obtain

$$n_{1,2}^{-2} = n_o^{-2} + \frac{1}{2}\left[(\zeta'_{11} + \zeta'_{22}) \pm \sqrt{(\zeta'_{11} - \zeta'_{22})^2 + (2\zeta'_{12})^2}\right].$$

Bearing in mind that $|\,\zeta'_{ij}\,| \ll 1$, we find the refractive indices according to rules of approximate calculations:

$$n_{1,2} = n_o\left\{1 - \frac{1}{4}n_o^2\left[(\zeta'_{11} + \zeta'_{22}) \pm \sqrt{(\zeta'_{11} - \zeta'_{22})^2 + (2\zeta'_{12})^2}\right]\right\}. \tag{78.14}$$

By definition birefringence Δ is equal to the absolute value of the difference between these refractive indices, i.e.

$$\Delta = \frac{1}{2}\,n_o^3\sqrt{(\zeta'_{11} - \zeta'_{12})^2 + (2\zeta'_{12})^2}. \tag{78.15}$$

This is the sought-for magnitude of the artificial birefringence for the case of the coincidence of light propagation with the optic axis of an unstressed crystal.

The induction vector $\boldsymbol{D}^{(1)}$ of a wave with the refractive index n_1 lies in the plane of the wave front and makes up angle φ with axis X'_1,

with

$$\tan\varphi = \frac{2\zeta'_{12}}{\zeta'_{11}-\zeta'_{22}+\sqrt{(\zeta'_{11}-\zeta'_{22})^2+(2\zeta'_{12})^2}}. \tag{78.16}$$

Vector $D^{(2)}$ also lies in the plane of the wave front and is perpendicular to vector $D^{(1)}$.

If a special reference frame is at once chosen so that $\zeta'_{12} = 0$ (sometimes it is successfully done for symmetry reasons), the birefringence

$$\Delta = \frac{1}{2} n_0^3 \mid \zeta'_{11} - \zeta'_{22} \mid, \tag{78.17}$$

and the directions of vibrations coincide with axes X'_1 and X'_2.

If the direction of light propagation does not coincide with the optic axis of a free crystal, the crystal's birefringence consists of the natural one, inherent in the free crystal, and of the artificial one caused by external influences. When the direction of light propagation makes up a sufficiently large angle with the optic axis of a free crystal, artificial birefringence is usually only a small increment to the natural one, and rules for approximate calculations can be used. We shall consider just this particular case.

Let us choose a special Cartesian reference frame $X'_1X'_2X'_3$ so that axis X'_3 coincides with the direction of light propagation, and axes X'_1 and X'_2, with the directions of vibrations (more precisely, with the directions of vectors D) of plane-polarized light waves propagating in a free crystal in the given direction. We denote the refractive indices of these waves n_{01} and n_{02} respectively. The equations of the central section of the optical indicatrix of the free crystal by the wave front plane in the special coordinate system have the following form

$$\left(\frac{x'_1}{n_{01}}\right)^2 + \left(\frac{x'_2}{n_{02}}\right)^2 = 1, \quad x'_3 = 0. \tag{78.18}$$

Just as the optical indicatrix serves as the characteristic surface of the three-dimensional tensor of dielectric impermeability, its central section by the wave front plane serves as the characteristic curve of the two-dimensional tensor—the projection of the tensor of dielectric impermeability onto this plane. For a free crystal the components of this tensor in the special coordinate system are

$$\begin{Vmatrix} n_{01}^{-2} & 0 \\ 0 & n_{02}^{-2} \end{Vmatrix}.$$

When an electric field or mechanical stresses are applied to the crystal, a small two-dimensional tensor

$$\begin{Vmatrix} \zeta'_{11} & \zeta'_{12} \\ \zeta'_{12} & \zeta'_{22} \end{Vmatrix}.$$

is added to the dielectric impermeability tensor. Here $\zeta'_{\alpha\beta}$ are the components of tensor ζ in the special coordinate system, see Sec. 77.

In Sec. 20 the changes are shown of the eigenvalues and eigenvectors of a symmetric second-rank tensor under a slight change of its components. Taking into account the connection between the eigenvalues of a two-dimensional tensor and the refractive indices, we find with the aid of (20.9) the inverse squares of the refractive indices

$$\begin{aligned} n_1^{-2} &= n_{01}^{-2} + \zeta'_{11}, \\ n_2^{-2} &= n_{02}^{-2} + \zeta'_{22} \end{aligned} \tag{78.19}$$

and the small angle of rotation of induction vectors $\boldsymbol{D}$ of light waves

$$\varphi = \omega_{12} = \frac{\zeta'_{12}}{n_{01}^{-2} - n_{02}^{-2}}. \tag{78.20}$$

A positive value of this angle corresponds to rotation about axis X'_3 from the positive end of axis X'_1 toward, again, the positive end of axis X'_2, while a negative value corresponds to rotation about the same axis, but in the opposite direction. With the aid of rules for approximate calculations, we find from (78.19) that

$$\begin{aligned} n_1 &= n_{01} - \frac{1}{2} n_{01}^3 \zeta'_{11}, \\ n_2 &= n_{02} - \frac{1}{2} n_{02}^3 \zeta'_{22}. \end{aligned} \tag{78.21}$$

Thus, under the action of external influences birefringence Δ of a crystal changes by the value

$$\Delta_{\text{art}} = \frac{1}{2} \left| n_{01}^3 \zeta'_{11} - n_{02}^3 \zeta'_{22} \right|. \tag{78.22}$$

In this case it is necessary to measure small changes of birefringence against the background of the spontaneous birefringence of the crystal, and these measurements are much more difficult than those made when light propagates along an optic axis.

In the use of formulas (78.14)-(78.17) and (78.20)-(78.22) it must be remembered that they are valid only in a special coordinate system which generally does not coincide with the crystal-physical system. To avoid laborious recalculation of the components of the third- and fourth-rank tensors under transition to a special coordinate system, the calculations can be most conveniently made in the following sequence:

(1) calculate components of the vector of the electric field intensity or of the stress tensor in the crystal-physical system of coordinates;

(2) with the aid of the tabulated values of tensors of the electrooptical or piezooptical coefficients find, by means of (77.3), (77.17) or (77.22), the components of tensor ζ in the crystal-physical coordinate system;

(3) calculate the components of tensor ζ in the special coordinate system;

(4) substitute their values into (78.14)-(78.17) or (78.20)-(78.22), calculate the value of artificial birefringence and determine the directions of vibrations.

Let us discuss some features of artificial birefringence in crystals of the cubic system and in isotropic bodies. In this case (78.15) gives the magnitude of artificial birefringence for any direction of light propagation. Tensor ζ is contained in this formula only in the form of the combination of the components $\zeta'_{11} - \zeta'_{22}$ and component ζ'_{12}. Hence it follows that the magnitude of artificial birefrin-

gence in optically isotropic bodies is influenced not by the spherical part but by the deviator of tensor ζ alone; its components are $\tilde{\zeta}_{ij} = \zeta_{ij} - 1/3\ \zeta_{kk}\delta_{ij}$. Since tensor ζ is determined by tensors of the Kerr coefficients, and of electrooptical and piezooptical coefficients, it must be found out to what degree the components of these tensors influence the magnitude of artificial birefringence and whether the components of latter tensors can be calculated from the results of measurement of artificial birefringence.

Let us begin with the discussion of electrooptical coefficients. Among optically isotropic media, only crystals of classes $\bar{4}3\,m$ and 23, have non-zero electrooptical coefficients $r_{41} = r_{52} = r_{63}$; other electrooptical coefficients of these crystals are zero. In case of the electrooptical effect $\tilde{\zeta}_{ij} = \tilde{r}_{ijk}E_k$ where

$$\tilde{r}_{ijk} = r_{ijk} - \frac{1}{3} r_{llk}\delta_{ij}, \tag{78.23}$$

or in contracted notation

$$\tilde{r}_{\lambda k} = \begin{cases} r_{\lambda k} - \frac{1}{3}(r_{1k} + r_{2k} + r_{3k}) & (\lambda = 1,\ 2,\ 3), \\ r_{\lambda k} & (\lambda = 4,\ 5,\ 6). \end{cases} \tag{78.24}$$

Substituting electrooptical coefficients differing from zero into (78.24), we become convinced that for crystals of the cubic system $\tilde{r}_{\lambda k} = r_{\lambda k}$, so that upon the measurement of artificial birefringence it is possible to determine the sole independent electrooptical coefficient of these crystals.

The determination of piezooptical coefficients and Kerr's coefficients from measurements of artificial birefringence is quite a different matter. Let us consider for definiteness the piezooptical coefficients; in this case $\tilde{\zeta}_{ij} = \pi_{ijkl}\sigma_{kl}$ were

$$\tilde{\pi}_{ijkl} = \pi_{ijkl} - \frac{1}{3}\pi_{mmkl}\delta_{ij}. \tag{78.25}$$

In contracted notation

$$\tilde{\pi}_{\lambda\mu} = \begin{cases} \pi_{\lambda\mu} - \frac{1}{3}(\pi_{1\mu} + \pi_{2\mu} + \pi_{3\mu}) & (\lambda = 1,\ 2,\ 3), \\ \pi_{\lambda\mu} & (\lambda = 4,\ 5,\ 6). \end{cases} \tag{78.26}$$

For the lower subsystem of the cubic system

$$\begin{aligned} \tilde{\pi}_{11} &= \frac{1}{3}(\pi_{11} - \pi_{12}) + \frac{1}{3}(\pi_{11} - \pi_{21}), \\ \tilde{\pi}_{12} &= -\frac{2}{3}(\pi_{11} - \pi_{12}) + \frac{1}{3}(\pi_{11} - \pi_{21}), \\ \tilde{\pi}_{21} &= \frac{1}{3}(\pi_{11} - \pi_{12}) - \frac{2}{3}(\pi_{11} - \pi_{21}), \\ \tilde{\pi} &= \pi_{44}. \end{aligned} \tag{78.27}$$

This means that, whatever the directions in which the artificial birefringence is measured, these measurements can only determine three independent combinations of the piezooptical coefficients: $\pi_{11} - \pi_{12}$, $\pi_{11} - \pi_{21}$ and π_{44}; on the other hand, these combinations are quite sufficient for the calculation of artificial birefringence caused by the piezooptical effect. The values of coefficients π_{11}, π_{12} and π_{21} taken separately are required for the calculation of the absolute values of the changes of refractive indices; they can be calculated from the results of the corresponding measurements. These measurements, however, are much more complicated than measurements of birefringence, since they involve not the polarization but interferometric methods.

In crystals of the higher subsystem of the cubic system $\pi_{21} = \pi_{12}$. Substituting this equality into (78.27), we find that

$$\begin{aligned} \tilde{\pi}_{11} &= \frac{2}{3}(\pi_{11} - \pi_{12}), \\ \tilde{\pi}_{12} &= -\frac{1}{3}(\pi_{11} - \pi_{12}), \\ \tilde{\pi}_{44} &= \pi_{44}. \end{aligned} \tag{78.28}$$

Thus, in this case measurements of artificial birefringence permit finding only the difference $\pi_{11} - \pi_{12}$, as well as coefficient π_{44}.

Finally, in isotropic bodies $\pi_{44} = \pi_{11} - \pi_{12}$, and this difference fully determines the artificial birefringence caused by the piezooptical effect in isotropic bodies.

The piezooptical effect in transparent isotropic bodies is extensively used for the following purpose: with the aid of the interference picture appearing due to artificial birefringence caused by a non-homogeneous stress field to restore the stress field that generated the picture. The corresponding application of the piezooptical effect can be found in the books by Cocker and Fylon (1931); Durelli and Ryley (1965); and Feupple and Mench (1966).

The description of the electrooptical effect and its applications is given in the works of Zheludev (1968, 1969, 1973); Mustel and Parygin (1970); Sonin and Vasilevskaya (1971); see also Perfilova, Sirotin and Sonin (1969), Voropayeva, Reznikov and Sirotin (1969).

Sec. 79. Non-Linear Polarization in Case of Propagation of Electromagnetic Intense Waves

The polarization of an anisotropic dielectric in strong harmonic fields consists of a principal, linear part $\boldsymbol{P}^{(1)}$ and small non-linear increments (quadratic $\boldsymbol{P}^{(2)}$, cubic $\boldsymbol{P}^{(3)}$ and so forth)

$$\boldsymbol{P} = \boldsymbol{P}^{(1)} + \boldsymbol{P}^{(2)} + \boldsymbol{P}^{(3)} + \ldots \tag{79.1}$$

Taking into consideration the dependence of polarizability on frequency, we shall register frequencies of the harmonic components of the electric field and polarization. Formally we can write that

$$\begin{aligned} P_i^{(1)}(\omega_1) &= \alpha_{ij}(\omega_1, \omega_2) E_j(\omega_2), \\ P_i^{(2)}(\omega_1) &= \chi_{ijk}(\omega_1, \omega_2, \omega_3) E_j(\omega_2) E_k(\omega_3), \\ P_i^{(3)}(\omega_1) &\quad \theta_{ijkl}(\omega_1, \omega_2, \omega_3, \omega_4) E_j(\omega_2) E_k(\omega_3) E_l(\omega_4). \end{aligned} \tag{79.2}$$

Tensors α, χ, θ are called the tensor of linear dielectric susceptibility, the tensor of quadratic susceptibility and the tensor of cubic susceptibility, respectively. Tensor $\alpha(\omega_1, \omega_2)$ gives the magnitude and direction of the linear part of the polarization with frequency ω_1, developed under the influence of the electric field with frequency ω_2; the tensor $\chi(\omega_1, \omega_2, \omega_3)$ determines the quadratic increment for polarization frequency ω_1 developed in the crystal under the influence of the interaction of two harmonic electric fields—one with frequency ω_2, another with frequency ω_3.

Let us point out, without derivation, an important property of susceptibility tensors *. These tensors generally have no internal symmetry, but their components will not change if the permutation of indices is accompanied by a simultaneous permutation of the corresponding frequencies:

$$\begin{aligned} \alpha_{ij}(\omega_1, \omega_2) &= \alpha_{ji}(\omega_2, \omega_1), \\ \chi_{ijk}(\omega_1, \omega_2, \omega_3) &= \chi_{ikj}(\omega_1, \omega_3, \omega_2) \\ &= \chi_{jik}(\omega_2, \omega_1, \omega_3) = \ldots, \\ \theta_{ijkl}(\omega_1, \omega_2, \omega_3, \omega_4) &= \theta_{jikl}(\omega_2, \omega_1, \omega_3, \omega_4) = \\ &\quad \theta_{kjil}(\omega_3, \omega_2, \omega_1, \omega_4) = \ldots \end{aligned} \tag{79.3}$$

The relations are trivial when obtained for permutations which did not involve the first index, and correspondingly the first frequency: it is obvious that fields $E_j(\omega_2)$, $E_k(\omega_3)$, $E_l(\omega_4)$ can be inserted into (79.2) in any sequence. Only those relations have physical meaning and call for proofs that result from permutations involving the first index and the first frequency, for example,

$$\chi_{ijk}(\omega_1, \omega_2, \omega_3) = \chi_{jik}(\omega_2, \omega_1, \omega_3).$$

If all the frequencies are different, these relations connect the components of different tensors and therefore do not point to internal symmetry. They determine the internal symmetry of tensors only in case of the coincidence of frequencies. For instance, the relation

$$\chi_{ijk}(\omega_1, \omega_2, \omega_2) = \chi_{ikj}(\omega_1, \omega_2, \omega_2)$$

* The derivation can be found in the works listed at the end of Sec. 80.

connects the components of one and the same tensor (not different tensors, as former relations) and shows that the latter is symmetric with respect to the last two indices, i.e. has internal symmetry $V[V^2]$.

For a clearly distinct formulation of (79.3), we wrote down the frequencies $\omega_1, \ldots, \omega_4$ without pondering over the degree to which they are independent. In reality the frequency of polarization is connected with the frequency of fields. If polarization is linearly dependent on field intensity, their frequencies will apparently coincide. This means that the tensor of linear susceptibility $\boldsymbol{\alpha}(\omega_1, \omega_2)$ differs from zero only when $\omega_1 = \omega_2$, so that it can be denoted as $\boldsymbol{\alpha}(\omega)$; evidently it is symmetric.

Let us derive frequency relations for the tensor of quadratic susceptibility $\chi(\omega_1, \omega_2, \omega_3)$. At any fixed point of a crystal the fields $\boldsymbol{E}(\omega_2)$ and $\boldsymbol{E}(\omega_3)$ depend on time according to the law

$$E_j(\omega_2) = A_j \cos \omega_2 t,$$

$$E_k(\omega_3) = B_k \cos(\omega_3 t + \varphi),$$

where φ is the phase shift between these fields at the given point. Since

$$E_j(\omega_2) E_k(\omega_3) = \frac{1}{2} A_j B_k \{\cos[(\omega_2 - \omega_3) t - \varphi] + \cos[(\omega_1 + \omega_2) t + \varphi]\},$$

the polarization quadratically dependent on the field has either a difference $(\omega_2 - \omega_3)$ or a summarized $(\omega_2 + \omega_3)$ frequency. In other words, tensor $\chi(\omega_1, \omega_2, \omega_3)$ differs from zero only in the following two cases:

$$\begin{aligned} \chi &= \chi(\omega_2 - \omega_3, \omega_2, \omega_3), \\ \chi &= \chi(\omega_2 + \omega_3, \omega_2, \omega_3). \end{aligned} \tag{79.4}$$

If across a crystal only monochromatic light with frequency ω is transmitted, intense enough for the quadratic polarization, $\omega_2 = \omega_3 = \omega_1$, to develop along with linear polarization, then expressions (79.4) become

$$\begin{aligned} \chi &= \chi(0, \omega, \omega), \\ \chi &= \chi(2\omega, \omega, \omega). \end{aligned} \tag{79.5}$$

Thus, the quadratic effects result in this case in the appearance of a constant component and of a second harmonic.

The same tensor $\chi(0, \omega, \omega)$ which determines the constant component in quadratic polarization also characterizes the electro-optical effect. Indeed, with account taken of the quadratic polarization, the induction vector of a light wave with frequency ω in a crystal located in an electrostatic field $\boldsymbol{E}(0)$ is equal to

$$D_i(\omega) = E_i(\omega) + 4\pi P_i(\omega) = E_i(\omega) + 4\pi P_i^{(1)}(\omega) + 4\pi P_i^{(2)}(\omega).$$

Denoting $\varkappa_{ij}(\omega) = \delta_{ij} + 4\pi\alpha_{ij}(\omega)$, we can write

$$D_i(\omega) = \varkappa_{ij}(\omega) E_j(\omega) + 4\pi\chi_{kij}(0, \omega, \omega) E_k(0) E_j(\omega).$$

The tensors of dielectric permittivity $\varkappa(\omega)$ and dielectric impermeability $\eta(\omega)$ are mutually reciprocal both with and without the electrostatic field $E(0)$:

$$\varkappa_{ij}(\omega)\eta_{jm}(\omega) = \delta_{im},$$

$$[\varkappa_{ij}(\omega) + 4\pi\chi_{kij}(0, \omega, \omega) E_k(0)][\eta_{jm}(\omega) + r_{jmk}(\omega) E_k(0)] = \delta_{im}.$$

With an accuracy up to terms of the second degree of smallness, this gives

$$\varkappa_{ij}(\omega) r_{jmk}(\omega) E_k(0) + 4\pi\chi_{kij}(0, \omega, \omega) E_k(0)\eta_{jm}(\omega) = 0,$$

whence it is not difficult to obtain formulas connecting the tensors of the electrooptical effect and quadratic susceptibility:

$$\begin{gathered} r_{lmk}(\omega) = -4\pi\chi_{kij}(0, \omega, \omega)\eta_{il}(\omega)\eta_{jm}(\omega), \\ \chi_{kij}(0, \omega, \omega) = -\frac{1}{4\pi}\varkappa_{il}(\omega)\varkappa_{jm}(\omega) r_{lmk}(\omega). \end{gathered} \tag{79.6}$$

Frequency relations for the cubic dielectric susceptibility result in the tensor $\theta(\omega_1, \omega_2, \omega_3, \omega_4)$ being non-zero only for frequencies

$$\begin{gathered} \omega_1 = \omega_2 + \omega_2 - \omega_4, \quad \omega_1 = \omega_2 - \omega_3 + \omega_4. \\ \omega_1 = -\omega_2 + \omega_3 + \omega_4, \quad \omega_1 = \omega_2 + \omega_3 + \omega_4. \end{gathered} \tag{79.7}$$

In particular, tensor $\theta(3\omega, \omega, \omega, \omega)$ specifies the generation of a third harmonic, tensor $\theta(0, 0, \omega, \omega)$—the Kerr effect, tensor $\theta(2\omega, 0, \omega, \omega)$, the generation of a second harmonic due to cubic polarization excited by a sufficiently strong electrostatic field.

Quadratic polarization is characterized by third-rank tensors, this meaning that it is possible only in non-centrosymmetric crystals. In particular, the generation of a second harmonic and the electrooptical effect are specified by tensors with internal symmetry $V[V^2]$, whose general form evidently coincides with the form of tensors of piezoelectric coefficients.

The effects of cubic polarization are, on the contrary, characterized by fourth-rank tensors and are therefore possible in media of any symmetry. In particular, the generation of a third harmonic is specified by a tensor with internal symmetry $V[V^3]$, the Kerr effect, by a tensor with internal symmetry $[V^2]^2$, and the generation of a second harmonic with the aid of an electrostatic field, by tensor $V^2[V^2]$. The general form of these tensors for all subsystems is given in Tables E.16, E.17, E.19, E.21 and E.22.

Sec. 80. Generation of Light Harmonics. Directions of Synchronism

When monochromatic light waves, with electric field intensities $\boldsymbol{E}(\omega_2)$ and $\boldsymbol{E}(\omega_3)$ are propagated across a transparent crystal with non-zero tensor of quadratic dielectric susceptibility, a quadratic electric polarization wave with a summary frequency

$$\boldsymbol{P}^{(2)}(\omega_2+\omega_3)=\chi(\omega_2+\omega_3,\ \omega_2,\ \omega_3):\ \boldsymbol{E}(\omega_2)\,\boldsymbol{E}(\omega_3) \tag{80.1}$$

develops in the crystal. This polarization can serve as a source of a light wave with a summary frequency. The actual formation of such a wave and the direction of its propagation depend on the conditions of interference: quadratic polarization developing at the given point of the crystal must intensify the wave with a summary frequency passing across this point. The conditions for constructive interference are most easily obtained when the formation of the wave with a summary frequency is considered to be the reaction between photons

$$\Phi(\omega_2,\ \boldsymbol{k}_2,\ \boldsymbol{d}_2)+\Phi(\omega_3,\ \boldsymbol{k}_3,\ \boldsymbol{d}_3)=\Phi(\omega_1,\ \boldsymbol{k}_1,\ \boldsymbol{d}_1); \tag{80.2}$$

here $\boldsymbol{k}$ is the wave vector of the corresponding photon, $\boldsymbol{d}$ is the unit vector of the direction of vibrations. In this reaction energy

$$\hbar\omega_2+\hbar\omega_3=\hbar\omega_1 \tag{80.3}$$

and momentum

$$\hbar\boldsymbol{k}_2+\hbar\boldsymbol{k}_3=\hbar\boldsymbol{k}_1. \tag{80.4}$$

must be conserved. The law of conservation of energy confirms that the resulting wave has a summary frequency, and from the law of conservation of momentum it follows that the wave also has a summary wave vector

$$\boldsymbol{k}_1=\boldsymbol{k}_2+\boldsymbol{k}_3. \tag{80.5}$$

Since

$$\boldsymbol{k}=\frac{\omega n(\omega,\ \boldsymbol{d})}{c}\boldsymbol{m},$$

where $\boldsymbol{m}$ is the unit vector of the wave normal, $n=n(\omega,\ \boldsymbol{d})$ is the refractive index, c is the light velocity in a vacuum, equality (80.5) can be rewritten as follows:

$$(\omega_2+\omega_3)\,n(\omega_2+\omega_3,\ \boldsymbol{d}_1)\,\boldsymbol{m}_1=\omega_2 n(\omega_2,\ \boldsymbol{d}_2)\,\boldsymbol{m}_2+\omega_3 n(\omega_3,\ \boldsymbol{d}_3)\,\boldsymbol{m}_3. \tag{80.6}$$

This is exactly the condition for constructive interference required for the formation of an intense wave with a summary frequency.

The condition of generation of a second harmonic is a special case of (80.6) when $\omega_2=\omega_3=\omega$:

$$n(2\omega,\ \boldsymbol{d}_1)\,\boldsymbol{m}_1=\frac{1}{2}\left[n(\omega,\ \boldsymbol{d}_2)\,\boldsymbol{m}_2+n(\omega,\ \boldsymbol{d}_3)\,\boldsymbol{m}_3\right]. \tag{80.7}$$

If the directions of vibrations ($\boldsymbol{d}_2 = \boldsymbol{d}_3 = \boldsymbol{d}$) in waves with basic frequency also coincide, this condition is simplified still more:

$$n\,(2\omega,\ \boldsymbol{d}_1)\,\boldsymbol{m}_1 = n\,(\omega,\ \boldsymbol{d})\,\frac{\boldsymbol{m}_2 + \boldsymbol{m}_3}{2}\ ; \tag{80.8}$$

in this case the wave vector of the second harmonic lies exactly midway between the wave vectors of the waves with basic frequency.

Finally, the condition of generation of a second harmonic by a single wave with a basic frequency is obtained from the above when $\boldsymbol{m}_2 = \boldsymbol{m}_3 = \boldsymbol{m}$:

$$n\,(2\omega,\ \boldsymbol{d}_1)\,\boldsymbol{m}_1 = n\,(\omega,\ \boldsymbol{d})\,\boldsymbol{m}. \tag{80.9}$$

Apparently, in this case $\boldsymbol{m}_1 = \boldsymbol{m}$, i.e. the direction of propagation of a second-harmonic wave coincides with the direction of propagation of the wave with a basic frequency.

The conditions for constructive interference (80.7), (80.8) and (80.9) required for the formation of a sufficiently intense wave of a second harmonic are satisfied only by a few directions called the *directions of synchronism*. In optically isotropic bodies, for example, they are most often absent at all. Indeed, for such bodies conditions (80.7) and (80.8) reduce to

$$n\,(2\omega)\,\boldsymbol{m}_1 = n\,(\omega)\,\frac{\boldsymbol{m}_2 + \boldsymbol{m}_3}{2}. \tag{80.10}$$

To fulfil condition (80.10) it is necessary that $n\,(2\omega) \leqslant n\,(\omega)$, but in case of normal dispersion the refractive index increases with frequency, so that this condition can be fulfilled only if between the frequencies ω and 2ω in the given optically isotropic non-linear medium there is an interval of anomalous dispersion, i.e. if there is an absorption line between these frequencies. From condition (80.9) for an optically isotropic body there follows the equality $n\,(2\omega) = n\,(\omega)$, which can be fulfilled only accidentally, even if with a fixed frequency ω there is an absorption band between the frequencies ω and 2ω.

In optically anisotropic crystals the directions of synchronism can exist even in the absence of the absorption lines between the frequencies ω and 2ω. Let us consider, for instance, the way of finding the directions of synchronism for the generation of a second harmonic by a single wave with a basic frequency in uniaxial crystals. In this case the equality

$$n\,(2\omega,\ \boldsymbol{d}_1) = n\,(\omega,\ \boldsymbol{d}) \tag{80.11}$$

must be fulfilled.

We shall seek for the directions of synchronism with the aid of surfaces of refractive indices. Due to dispersion, different surfaces of refractive indices correspond to different frequencies; in case of

normal dispersion the surface which corresponds to a higher frequency has greater dimensions.

If the surfaces of refractive indices for the frequencies ω and 2ω (their sections are shown in Fig. 80.1) are drawn on a common axis and with a common centre, the straight lines, connecting the centre with the circumference along which these surfaces intersect, will be the directions of synchronism. These directions form a circular cone whose axis is parallel to the optic axis of the crystal. In case

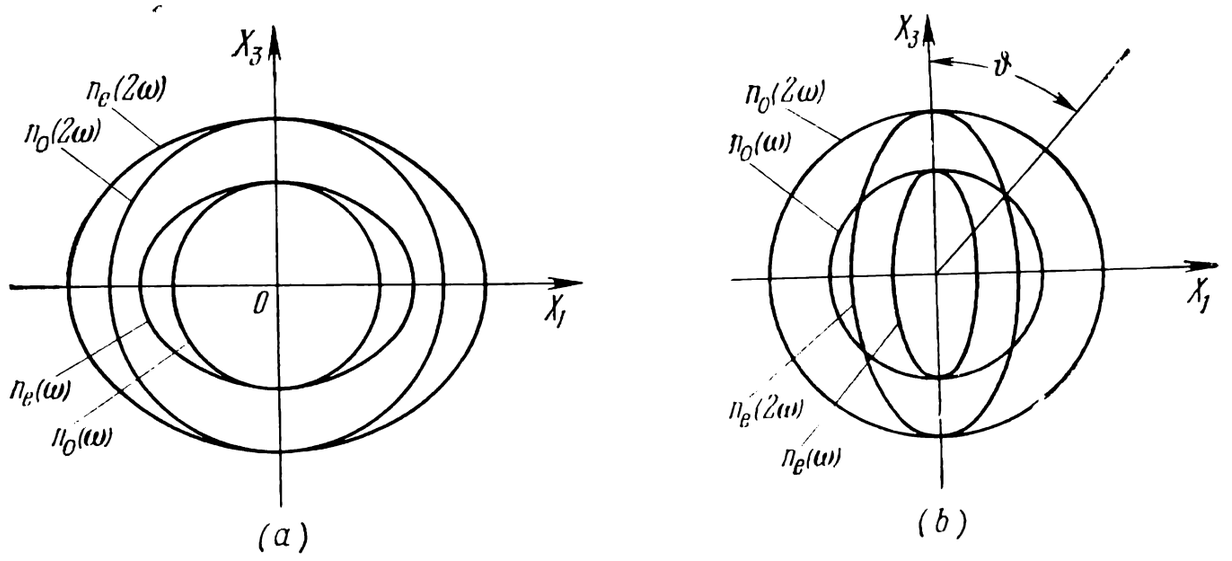


Fig. 80.1. Sections of the surface of the refractive indices of uniaxial crystals: (a) the crystal is optically positive, there are no directions of synchronism; (b) the crystal is optically negative, the available directions of synchronism make up angle ϑ with the optic axis

of low optical anisotropy (or a too great dispersion) these surfaces will not intersect; this means that the crystal has no directions of synchronism for doubling the given frequency.

Fig. 80.1 makes it apparent that for optically positive and negative crystal the directions of synchronism are determined from the following conditions respectively*:

$$n_e(\omega) = n_o(2\omega), \tag{80.12$^+$}$$

$$n_o(\omega) = n_e(2\omega); \tag{80.12$^-$}$$

in both cases the two waves satisfying the condition of synchronism are polarized in mutually perpendicular directions. In optically uniaxial crystals the refractive index of an ordinary wave n_o does not depend on the direction of propagation: $n_o = N_o$, while the refractive index of an extraordinary wave n_e depends on the angle ϑ between the direction of its propagation and the optic axis: $n_e^{-2} =$

* Further on in this Section, similar, but not coinciding, formulas for optically positive ($N_e > N_o$) and optically negative ($N_e < N_o$) crystals are denoted by superscripts + and — placed after the number of the formula.

$= N_e^{-2} \sin^2 \vartheta + N_o^{-2} \cos^2 \vartheta$; here N_o and N_e are the main refractive indices (see Sec. 35). Substituting these values into (80.12) we shall find upon simple calculations the angle ϑ between the direction of synchronism and the optic axis of the crystal:

$$\sin \vartheta = \sqrt{\frac{N_o^{-2}(\omega) - N_o^{-2}(2\omega)}{N_o^{-2}(\omega) - N_e^{-2}(\omega)}}, \tag{80.13$^+$}$$

$$\sin \vartheta = \sqrt{\frac{N_o^{-2}(\omega) - N_o^{-2}(2\omega)}{N_o^{-2}(2\omega) - N_o^{-2}(2\omega)}}. \tag{80.13$^-$}$$

If the value of $\sin \vartheta$, calculated according to the corresponding formula (80.13), does not exceed unity in absolute value, as the case should be, then the given crystal has a whole circular cone of directions of synchronism: the condition of synchronism is satisfied correspondingly by the extraordinary or the ordinary wave with frequency ω, propagating in this crystal in the direction

$$\boldsymbol{m} = (\boldsymbol{e}_1 \cos \varphi + \boldsymbol{e}_2 \sin \varphi) \sin \vartheta + \boldsymbol{e}_3 \cos \vartheta, \tag{80.14}$$

where $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$ are the mutually perpendicular unit vectors of the crystal-physical system of coordinates, angle φ is arbitrary, and angle ϑ is determined by formulas (80.13). However, this wave must also generate quadratic polarization, and of such a direction that the wave with doubled frequency is polarized perpendicularly to the primary wave.

The direction of the electric field vector $\boldsymbol{E}$ in the ordinary wave coincides with the direction of the electric induction vector $\boldsymbol{D}$. The unit vector of this direction for the wave whose normal is determined with the aid of (80.14) is

$$\boldsymbol{e}_0 = \boldsymbol{d}_0 = \boldsymbol{e}_1 \sin \varphi - \boldsymbol{e}_2 \cos \varphi. \tag{80.15}$$

As for the extraordinary wave, the unit vectors of electric induction $\boldsymbol{d}_e$ and the electric field intensity $\boldsymbol{e}_e$ are different and equal respectively to

$$\boldsymbol{d}_e = (\boldsymbol{e}_1 \cos \varphi + \boldsymbol{e}_2 \sin \varphi) \cos \vartheta - \boldsymbol{e}_3 \sin \vartheta, \tag{80.16}$$

$$\boldsymbol{e}_e = A\,(N_o^{-2}(\boldsymbol{e}_1 \cos \varphi + \boldsymbol{e}_2 \sin \varphi) \cos \vartheta - N_e^{-2} \boldsymbol{e}_3 \sin \vartheta], \tag{80.17}$$

$$A = 1/\sqrt{N_o^{-4} \cos^2 \vartheta + N_e^{-4} \sin^2 \vartheta}. \tag{80.18}$$

The wave of double frequency is generated by the component $\boldsymbol{e}\,(2\omega) \times \boldsymbol{P}\,(2\omega)$ of the vector of quadratic polarization $\boldsymbol{P}\,(2\omega)$ in the direction of the electric field vector in a second-harmonic wave $\boldsymbol{e}\,(2\omega)$; this component is equal to the square of the electric field strength in the wave with the basic frequency $E^2 = E^2\,(\omega)$ multiplied respectively by one of the contractions of the tensor of quadratic

susceptibility $\chi = \chi(2\omega, \omega, \omega)$ with unit vectors e_o and e_e:

$$e_o \cdot \chi : e_e e_e = A^2 \{ N_o^{-4} \cos^2 \vartheta [\chi_{12} \sin^3 \varphi - (\chi_{22} - \chi_{16}) \sin^2 \varphi \cos \varphi + (\chi_{11} - \chi_{26}) \sin \varphi \cos^2 \varphi - \chi_{21} \cos^3 \varphi] - N_o^{-2} N_e^{-2} \sin \vartheta \cos \vartheta [\chi_{14} \sin^2 \varphi + (\chi_{15} - \chi_{24}) \sin \varphi \cos \varphi - \chi_{25} \cos^2 \varphi] + N_e^{-4} \sin^2 \vartheta [\chi_{13} \sin \varphi - \chi_{23} \cos \varphi] \}, \quad (80.19^+)$$

$$e_e \cdot \chi : e_o e_o = A \{ N_o^{-2} \cos \vartheta [\chi_{21} \sin^3 \varphi + (\chi_{11} - \chi_{26}) \sin^2 \varphi \cos \varphi + (\chi_{22} - \chi_{16}) \sin \varphi \cos^2 \varphi + \chi_{12} \cos^3 \varphi] - N_e^{-2} \sin \vartheta [\chi_{31} \sin^2 \varphi - \chi_{36} \sin \varphi \cos \varphi + \chi_{32} \cos^2 \varphi] \}. \quad (80.19^-)$$

These contractions can be imagined to be the components χ'_{122} and χ'_{211} of tensor χ in a special coordinate system $X'_1 X'_2 X'_3$ whose axes are $X'_1 \parallel e_0$, $X'_2 \parallel e_e$. The coefficients of quadratic susceptibility $\chi_{i\mu}$ in formulas (80.19) are determined by the recalculation rules*

$$\chi_{i\mu} = \begin{cases} \chi_{ikl} & (kl \leftrightarrow \mu = 1, 2, 3), \\ 2\chi_{ikl} & (kl \leftrightarrow \mu = 4, 5, 6), \end{cases} \quad (80.20)$$

which correspond to the general recalculation rules for the dyad $(EE)_\mu$:

$$(EE)_\mu = E_k E_l \quad (kl \leftrightarrow \mu = 1, \ldots, 6).$$

Let us substitute into (80.19) the values of the coefficients $\chi_{i\mu}$ for each of the piezoelectric classes of the intermediate category and tabulate the results (Table (80.1)).

Table 80.1 shows that negative crystals of classes 422, 622 and $\infty 2$ and positive crystals of classes $4mm$, $6mm$, and ∞m are completely unfit for the generation of a second harmonic. Actually, there are still more classes unfit for the generation of a second harmonic. The point is that tensor $\chi(2\omega, \omega, \omega)$ is not symmetric with respect to indices solely because of dispersion. If the crystal is transparent within the whole range of frequencies (ω-2ω) the dispersion in this range is low and tensor $\chi(2\omega, \omega, \omega)$ is close to the symmetrized tensor $\tilde{\chi}_{ikl} = \chi_{(ikl)}$. Having calculated the contractions given in Table 80.1 for the symmetrized tensor $\tilde{\chi}$ we shall see that positive crystals of classes 4, 6, ∞, 422, 622, $\infty 2$ are also practically inapplicable for the generation of the second harmonic.

Most advantageous for the generation of a second harmonic are such directions of synchronism which lead to the maximum value of the corresponding tabulated expression. For example, in optically negative uniaxial crystals of potassium dihydrophosphate (KDP) and ammonium dihydrophosphate (ADP)—class $\bar{4}2m$—used

* They are the same as for piezoelectric coefficients $d_{i\mu}$. The same recalculation rules for the coefficients $\chi_{i\mu}$ were adopted by Akhmanov and Khokhlov (1964) and Bloembergen (1966).

Table 80.1

The Component of the Vector of Quadratic Polarization in the Direction of the Electric Field Strength of a Second-Harmonic Wave

Classes	Function $F = F(\chi, N, \vartheta, \varphi)$	
	Positive crystals: $e(2\omega)\cdot P(2\omega) = A^2F$, $N = N(\omega)$	Negative crystals: $e(2\omega)\cdot P(2\omega) = AF$, $N = N(2\omega)$
3	$N_o^{-4}\cos^2\vartheta(\chi_{11}\sin 3\varphi + \chi_{22}\cos 3\varphi) - \frac{1}{2}N_o^{-2}N_e^{-2}\chi_{14}\sin 2\vartheta$	$N_o^{-2}\cos\vartheta(\chi_{22}\sin 3\varphi - \chi_{11}\cos 3\varphi) - N_e^{-2}\chi_{31}\sin\vartheta$
32	$N_o^{-4}\chi_{11}\cos^2\vartheta\sin 3\varphi - \frac{1}{2}N_o^{-2}N_e^{-2}\chi_{14}\sin 2\vartheta$	$-N_o^{-2}\chi_{11}\cos\vartheta\cos 3\varphi$
$3m$	$N_o^{-4}\chi_{22}\cos^2\vartheta\cos 3\varphi$	$N_o^{-2}\chi_{22}\cos\vartheta\sin 3\varphi - N_e^{-2}\chi_{31}\sin\vartheta$
4, 6, ∞	$-\frac{1}{2}N_o^{-2}N_e^{-2}\chi_{14}\sin 2\vartheta$	$-N_e^{-2}\chi_{31}\sin\vartheta$
422, 622, $\infty 2$	$-\frac{1}{2}N_o^{-2}N_e^{-2}\chi_{14}\sin 2\vartheta$	0
$4mm$, $6mm$, ∞m	0	$-N_e^{-2}\chi_{31}\sin\vartheta$
$\bar{4}$	$\frac{1}{2}N_o^{-2}N_e^{-2}\sin 2\vartheta \times (\chi_{14}\cos 2\varphi + \chi_{24}\sin 2\varphi)$	$N_e^{-2}\sin\vartheta\left(\chi_{31}\cos 2\varphi + \frac{1}{2}\chi_{36}\sin 2\varphi\right)$
$42m$	$\frac{1}{2}N_o^{-2}N_e^{-2}\chi_{14}\sin 2\vartheta\cos 2\varphi$	$\frac{1}{2}N_e^{-2}\chi_{36}\sin\vartheta\sin 2\varphi$
$\bar{6}$	$N_o^{-4}\cos^2\vartheta(\chi_{11}\sin 3\varphi + \chi_{22}\cos 3\varphi)$	$N_o^{-2}\cos\vartheta(\chi_{22}\sin 3\varphi - \chi_{11}\cos 3\varphi)$
$\bar{6}m2$	$N_o^{-4}\chi_{22}\cos^2\vartheta\cos 3\varphi$	$N_o^{-2}\chi_{22}\cos\vartheta\sin 3\varphi$

for doubling the frequency of laser emission, the maximum of the tabulated expression is attained when $\varphi = 45°$. It can be seen from (80.14) that this corresponds to the direction of the wave normal

$$\boldsymbol{m} = \frac{1}{\sqrt{2}}(\boldsymbol{e}_1 + \boldsymbol{e}_2)\sin\vartheta - \boldsymbol{e}_3\cos\vartheta.$$

The non-centrosymmetric biaxial crystals are also suitable for the generation of a second harmonic; from the standpoint of crystal

physics they are even more preferable than the uniaxial ones, since they offer a more varied choice of directions. In this case, however, the analysis of the arising possibilities is much more complicated, and it appears to be more expedient to conduct it not in a general form which leads to very cumbersome formulas, but for each crystal separately (cf. Orlov, 1969).

The crystal-physical aspect of generation of a third harmonic is investigated similarly. Since the tensor θ which determines it is of an even type, crystals of the centrosymmetric classes can also be used for the generation of a third harmonic, while the symmetry of this effect is influenced only by the subsystem, but not by the class of the crystal.

In the last two sections we discussed only the crystal-physical nature of some of the simplest problems of non-linear optics. Generally, for the non-linear optics see Akhmanov and Khokhlov (1964); Akhmanov (1969); Blombergen (1966); Klimontovich (1966); Pekkara (1973); Schubert and Wilhelmi (1973).

Sec. 81. Optical Activity of Crystals

In all condensed media, including crystals, *spatial dispersion* occurs: the vector of electric polarization $\boldsymbol{P}(\boldsymbol{r}, t)$ is determined not only by the value of the electric field vector $\boldsymbol{E}$ at the same point $\boldsymbol{r}$, but also by its values in the vicinity of this point. If the electric field were homogeneous, its values in the vicinity of the point $\boldsymbol{r}$ would be the same as at the point $\boldsymbol{r}$ itself, and no spatial dispersion would be observed. Therefore, spatial dispersion can be conceived as the dependence of the vector of electric polarization $\boldsymbol{P}$ not only on vector $\boldsymbol{E}$ itself, but also on its spatial derivatives. Restricting ourselves to the first terms of the expansion, we obtain

$$P_i = \alpha_{ij} E_j + \beta_{ijk} \frac{\partial E_j}{\partial x_k}, \qquad \boldsymbol{P} = \boldsymbol{\alpha} \cdot \boldsymbol{E} + \boldsymbol{\beta} : \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{r}}. \tag{81.1}$$

In crystals with tensor $\boldsymbol{\beta}$ differing from zero there occurs the spatial dispersion of the first order; such crystals are called *optically active*. The spatial dispersion in other crystals can only be of the second order: the polarization in such crystals depends not on the first, but on the second spatial derivatives of intensity alone. We shall confine ourselves to the optical activity (on the influence of the spatial dispersion of the second order on the optical properties of crystals see Agranovich and Ginsburg, 1979).

In crystal optics it is more convenient to examine the relation between the electric field intensity $\boldsymbol{E}$ and the electric induction $\boldsymbol{D}$;

then instead of (81.1), we use

$$E_i = \eta_{ij} D_j + \gamma_{ijk} \frac{\partial D_j}{\partial x_k}, \qquad \boldsymbol{E} = \boldsymbol{\eta} \cdot \boldsymbol{D} + \boldsymbol{\gamma} : \frac{\partial \boldsymbol{D}}{\partial \boldsymbol{r}}. \tag{81.2}$$

Since for a monochromatic wave with the wave vector $\boldsymbol{k}$ the derivative $\partial \boldsymbol{D}/\partial \boldsymbol{r} = i\boldsymbol{D}\boldsymbol{k}$, (81.2) in this case becomes

$$E_j = (\eta_{jl} + i\gamma_{jlm} k_m) D_l, \quad \boldsymbol{E} = (\boldsymbol{\eta} + i\boldsymbol{\gamma} \cdot \boldsymbol{k}) \cdot \boldsymbol{D}. \tag{81.3}$$

The expression in brackets plays the role of a somewhat altered tensor of dielectric impermeability. Thus spatial dispersion results in the dependence of the tensor of dielectric impermeability on the wave vector, just as the ordinary, i.e. time, or frequency dispersion leads to the dependence of this tensor on frequency. (81.3) shows that the increment to the tensor of dielectric impermeability, linearly dependent on the wave vector, is pure imaginary. Insofar as the wave vector $\boldsymbol{k}$ is inversely proportional to the wavelength λ (actually, $\boldsymbol{k} = (2\pi/\lambda)\, \boldsymbol{m}$, where $\boldsymbol{m}$ is the unit vector of the wave normal), the increment is also inversely proportional to λ. But since the only characteristic of an infinite crystal with a length dimensionality is the dimension of the elementary cell a, it is apparent that the order of this increment is a/λ.

For the frequencies at which the crystal is transparent, the tensor of dielectric impermeability $\boldsymbol{\eta}$ is Hermitian, i.e. its real part is symmetric and the imaginary one is antisymmetric (see Landau and Lifshits, 1957, Sec. 76, formula (76.4) and Agranovich and Ginsburg, 1979, Sec. 1, formula (1.21)). It follows that tensor $\boldsymbol{\gamma}$ is antisymmetric with respect to the first two indices

$$\gamma_{jlm} = -\gamma_{ljm}, \tag{81.4}$$

i.e. its internal symmetry is $\{V^2\}\, V$. The relation of duality

$$\{V^2\}\, V \sim \varepsilon V^2 \tag{81.5}$$

allows to introduce the *pseudotensor of gyration* $\mathbf{G}$, dual of tensor $\boldsymbol{\gamma}$ up to the scalar factor $\lambda/(2\pi)$:

$$G_{ln} = \frac{\pi}{\lambda} \delta_{lij} \gamma_{ijn}, \qquad \frac{2\pi}{\lambda} \gamma_{ijn} = \delta_{ijl} G_{ln}; \tag{81.6}$$

thereupon relation (81.3) is written thus:

$$E_j = (\eta_{jk} + i\delta_{jkl} G_{ln} m_n) D_k, \quad \boldsymbol{E} = \boldsymbol{\eta} \cdot \boldsymbol{D} + i\boldsymbol{D} \times \mathbf{G} \cdot \mathbf{m}. \tag{81.7}$$

Let us find out what plane waves can propagate in a medium characterized by material equation (81.7). For this purpose we introduce a right-hand system of coordinates, the axis X_3 of which is directed along the vector of the wave normal $\boldsymbol{m}$, while the axes X_1 and X_2 coincide with the principal axes of the central section of the optical indicatrix of the crystal by the wave-front plane: X_1 coincides with

the major principal axis, X_2, with the minor one. In this system of coordinates the first two equations (81.7) become

$$\begin{aligned} E_1 &= n_{01}^{-2} D_1 + iG_{33} D_2, \\ E_2 &= -iG_{33} D_1 + n_{02}^{-2} D_2. \end{aligned} \tag{81.8}$$

In the chosen system of coordinates $D_3 = 0$ and $\eta_{12} = 0$, while $\eta_{11} = n_{01}^{-2}$ and $\eta_{22} = n_{02}^{-2}$; here n_{01} and n_{02} are the refractive indices of waves which would propagate in the given direction if there were no spatial dispersion, and $n_{01} \geqslant n_{02}$.

As is known, from Maxwell's equations for plane electromagnetic waves it follows that

$$\boldsymbol{E} - \boldsymbol{mm} \cdot \boldsymbol{E} = n^{-2} \boldsymbol{D} \tag{81.9}$$

(see Sec. 34). In our coordinate system this means that $E_1 = n^{-2} D_1$ and $E_2 = n^{-2} D_2$. Therefore we eliminate E_1 and E_2 from (81.8):

$$\begin{aligned} (n_{01}^{-2} - n^{-2})\, D_1 + iG_{33} D_2 &= 0, \\ -iG_{33} D_1 + (n_{02}^{-2} - n^{-2})\, D_2 &= 0. \end{aligned} \tag{81.10}$$

The obtained system of the homogeneous linear equations with respect to the components of the induction vector has an untrivial solution only in case its determinant vanishes:

$$(n_{01}^{-2} - n^{-2})(n_{02}^{-2} - n^{-2}) - G_{33}^2 = 0. \tag{81.11}$$

Let us consider the quantity

$$\rho = \frac{1}{2G_{33}} \left[\sqrt{(n_{02}^{-2} - n_{01}^{-2})^2 + (2G_{33})^2} - (n_{02}^{-2} - n_{01}^{-2}) \right]. \tag{81.12}$$

From the earlier condition $n_{01} \geqslant n_{02}$ there follows the inequality $|\rho| \leqslant 1$, the sign of ρ coinciding with the sign of G_{33}. It is easily verified that the solutions of quadratic equation (81.11) are

$$\begin{aligned} n_1^{-2} &= n_{01}^{-2} - \rho G_{33}, \\ n_2^{-2} &= n_{02}^{-2} + \rho G_{33}. \end{aligned} \tag{81.13}$$

Since $|G_{33}| \ll 1$, while n_{01} and n_{02} are numbers of the order of unity, the refractive indices n_1 and n_2 are with sufficient accuracy equal to

$$\begin{aligned} n_1 &= n_{01} + \frac{1}{2} n_{01}^3 \rho G_{33}, \\ n_2 &= n_{02} - \frac{1}{2} n_{02}^3 \rho G_{33}. \end{aligned} \tag{81.14}$$

Substituting into (81.10) solutions n_1^{-2} and n_2^{-2} from (81.13), let us find the ratios of the components of the induction vectors $\boldsymbol{D}^{(1)}$ and $\boldsymbol{D}^{(2)}$ for waves propagating with velocities c/n_1 and c/n_2

respectively

$$\frac{D_2^{(1)}}{D_1^{(1)}} = \frac{D_1^{(2)}}{D_2^{(2)}} = i\rho. \tag{81.15}$$

The general form of vectors $\boldsymbol{D}^{(1)}$ and $\boldsymbol{D}^{(2)}$ satisfying relations (81.15) is

$$\begin{aligned} \boldsymbol{D}^{(1)} &= D^{(1)}(\boldsymbol{e}_1 + i\rho\boldsymbol{e}_2)\exp[i(k^{(1)}x_3 - \omega t + \varphi^{(1)})], \\ \boldsymbol{D}^{(2)} &= D^{(2)}(i\rho\boldsymbol{e}_1 + \boldsymbol{e}_2)\exp[i(k^{(2)}x_3 - \omega t + \varphi^{(2)})], \end{aligned} \tag{81.16}$$

where $\boldsymbol{D}^{(\alpha)}\exp(i\varphi^{(\alpha)})$ is a complex amplitude, and $k^{(\alpha)} = \omega n_\alpha / c$ ($\alpha = 1, 2$). The electric induction vectors are the real parts of these complex vectors:

$$\begin{aligned} \operatorname{Re}\boldsymbol{D}^{(1)} &= D^{(1)}[\boldsymbol{e}_1\cos(k^{(1)}x_3 - \omega t + \varphi^{(1)}) - \rho\boldsymbol{e}_2\sin(k^{(1)}x_3 - \omega t + \varphi^{(1)})], \\ \operatorname{Re}\boldsymbol{D}^{(2)} &= D^{(2)}[-\rho\boldsymbol{e}_1\sin(k^{(2)}x_3 - \omega t + \varphi^{(2)}) + \\ &\qquad + \boldsymbol{e}_2\cos(k^{(2)}x_3 - \omega t + \varphi^{(2)})]. \end{aligned} \tag{81.17}$$

At any fixed point in space the ends of the induction vectors, determined by these equalities, describe ellipses lying in the wave-front plane $x_3 = \text{const}$ during time $T = 2\pi/\omega$. Indeed, equalities (81.17) can be expressed respectively as

$$\begin{cases} \operatorname{Re} D_1^{(1)} = D^{(1)}\cos(\omega t - \psi^{(1)}), \\ \operatorname{Re} D_2^{(1)} = \rho D^{(1)}\sin(\omega t - \psi^{(1)}); \end{cases} \tag{81.18}$$

$$\begin{cases} \operatorname{Re} D_1^{(2)} = \rho D^{(2)}\sin(\omega t - \psi^{(2)}), \\ \operatorname{Re} D_2^{(2)} = D^{(2)}\cos(\omega t - \psi^{(2)}), \end{cases}$$

where $\psi^{(\alpha)} = k^{(\alpha)}x_3 + \varphi^{(\alpha)}$. Formulas (81.18) are the parametric equations of ellipses with the ratio between the minor and the major axes being $|\rho|$ (this ratio is usually called *ellipticity*). Table 81.1 shows the ellipses circumscribed by the ends of vectors Re $\boldsymbol{D}^{(1)}$ and Re $\boldsymbol{D}^{(2)}$.

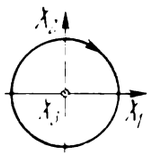
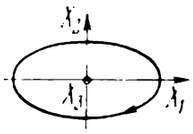
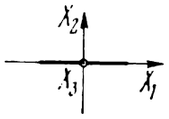
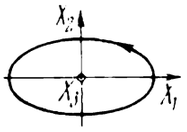
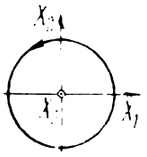
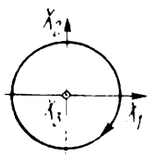
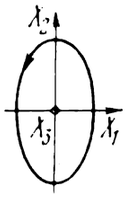
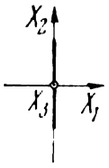
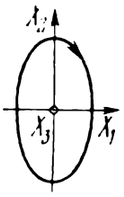
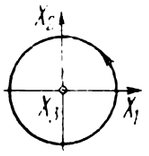
Thus, the two electromagnetic waves propagating in an optically active crystal in the direction in which the normal component of the pseudotensor of gyration differs from zero, are elliptically polarized; their polarization ellipses have the same axial ratio but are rotated by 90° with respect to one another and the circuits about them are made in the opposite directions.

The elliptic polarization is called *right-handed* if from the viewpoint of the observer looking toward the light vector $\boldsymbol{D}$ rotates clockwise, and *left-handed* if the vector rotates counterclockwise*; Table

* This traditional definition of the right- and left-handed polarization is used in the majority of manuals (Shubnikov, Flint and Bokyi, 1940; Landsberg, 1957; Landau and Lifshits, 1957; F. I. Fedorov, 1958; Shubnikov, 1958; Nye,

Table 81.1

Polarization of Light Waves for Different Values of Parameter ρ
(the second wave propagates
at a higher velocity than the first wave ($n_2 < n_1$)).

G_{33}	$G_{33} < 0$		$G_{33} = 0$	$G_{33} > 0$	
ρ	$\rho = -1$	$-1 < \rho < 0$	$\rho = 0$	$0 < \rho < 1$	$\rho = 1$
Re $D^{(1)}$					
Re $D^{(2)}$					

81.1 shows that when $G_{33} > 0$, the wave with the velocity higher than that of ($D^{(2)}$) has a right-handed polarization, and when $G_{33} < 0$, a left-handed polarization.

Optical activity is highly pronounced when light propagates along the optic axis of a crystal. Then $n_{01} = n_{02} = n_0$ and

$$\rho = \frac{|G_{33}|}{G_{33}} = \operatorname{sign} G_{33} = \begin{cases} 1, & \text{if} \quad G_{33} > 0, \\ -1, & \text{if} \quad G_{33} < 0. \end{cases} \tag{81.19}$$

Equalities (81.18) become in this case parametric equations of circumferences. Therefore, along the optic axes of optically active crystals circularly polarized waves propagate. Their refractive indices, according to (81.14) and (81.19) are

$$\begin{aligned} n_1 &= n_0 + \frac{1}{2} n_0^3 \, |G_{33}|, \\ n_2 &= n_0 - \frac{1}{2} n_0^3 \, |G_{33}|. \end{aligned} \tag{81.20}$$

1957). Recently a converse definition has come into use (Landau and Lifshits, 1973; Berestetsky, Lifshits and Pitayevsky, 1968; Feynman, Leyton and Sands, 1964, issue 3). According to the traditional definition, the end of the vector D, during the propagation of a right-handed polarized wave, moves in space in the direction of a left-handed screw; the new definition is free of this disadvantage.

In this case too, when $G_{33} > 0$, the right-hand-polarized wave propagates with a higher velocity, and when $G_{33} < 0$ the left-hand-polarized wave has a higher velocity. The refractive index of the left-hand circularly polarized wave is denoted by n_l or n_g (by the first letters of the English word 'left' or the French word 'gauche'), and that of the right-hand wave, by n_r or n_d (from English 'right' or French 'droit'). Evidently

$$n_l = n_0 + \frac{1}{2} n_0^3 G_{33},$$
$$n_r = n_0 - \frac{1}{2} n_0^3 G_{33}. \tag{81.21}$$

If the birefringence of a crystal is not too small, the ellipticity of the wave $|\rho|$ decreases rapidly with the divergence of the wave normal from the optic axis of the crystal. When the terms in the radicand in (81.12) become equal to each other, $|\rho| = \sqrt{2} - 1 \approx \approx 0.414$. It can be easily calculated that in optically uniaxial crystals this value of ellipticity is attained when the wave normal diverges by the angle ϑ defined by the equality

$$\sin \vartheta = \sqrt{\left| \frac{2G_{33}}{N_e^{-2} - N_o^{-2}} \right|}. \tag{81.22}$$

Since G_{33} has an order of magnitude of 10^{-4}-10^{-5}, and $|N_e^{-2} - N_o^{-2}|$ usually constitutes several hundredths, the angle ϑ does not exceed a few degrees. This assessment can also be applied to biaxial crystals. When the wave normal diverges still further from the optic axis, the ellipticity becomes very small, and can be calculated by an approximate formula

$$\rho = \frac{G_{33}}{n_{02}^{-2} - n_{01}^{-2}} \tag{81.23}$$

instead of (81.12). Thus, in the majority of directions elliptically polarized light waves propagating in birefringent optically active crystals are close to linearly polarized ones. On the contrary, in optically active cubic crystals and isotropic bodies all light waves are circularly polarized.

Let us investigate linearly polarized light normally incident on a transparent plane-parallel plate of thickness d, cut out of an optically active crystal perpendicularly to its optic axis. Let us introduce a right-hand Cartesian system of coordinates, X_1, X_2, X_3 so that axis X_3 is directed along the wave normal, and axis X_1 coincides with the direction of vibrations of light incident on the plate. Let $x_3 = 0$ be the front (with respect to the direction of light propagation) surface of the plate, and $x_3 = d$, the back surface.

The electric induction vector of the light wave vibrates according to the law $\boldsymbol{e}_1 \cos \omega t$ directly before the crystal. Upon entering the

crystal the wave breaks up into two circularly polarized waves of equal intensity: the left-hand wave has the direction of the induction vector

$$\boldsymbol{e}_1 \cos (k^{(l)} x_3 - \omega t) - \boldsymbol{e}_2 \sin (k^{(l)} x_3 - \omega t),$$

while the right-hand wave

$$\boldsymbol{e}_1 \cos (k^{(r)} x_3 - \omega t) + \boldsymbol{e}_2 \sin (k^{(r)} x_3 - \omega t);$$

their velocities being $\omega/k^{(l)}$ and $\omega/k^{(r)}$ respectively. Upon passing across the plate these light waves will again merge into a single wave whose vibrations directly beyond the plate are characterized by the vector

$$\boldsymbol{e}_1 [\cos (k^{(l)} d - \omega t) + \cos (k^{(r)} d - \omega t)] - \\ - \boldsymbol{e}_2 [\sin (k^{(l)} d - \omega t) - \sin (k^{(r)} d - \omega t)].$$

Having done the elementary trigonometric transformations and taken into account that $k^{(l)} + k^{(r)} = 2\omega n_0/c$, while $k^{(l)} - k^{(r)} = 2\pi n_0^3 G_{33}/\lambda_0$, where $n_0 = 1/2\,(n_l + n_r)$ is the mean refractive index for light propagating along the optic axis, and λ_0 is the wavelength in vacuum, we obtain the vector of the direction of vibrations of the wave leaving the plate:

$$\left(\boldsymbol{e}_1 \cos \frac{\pi n_0^3 G_{33} d}{\lambda_0} - \boldsymbol{e}_2 \sin \frac{\pi n_0^3 G_{33} d}{\lambda_0}\right) \cos \left[\omega \left(t - \frac{n_0 d}{c}\right)\right].$$

This means that having left the crystal the wave is also linearly polarized, but the polarization vector has rotated from its initial position by the angle

$$\psi = \frac{\pi n_0^3 G_{33} d}{\lambda_0} \tag{81.24}$$

in the clockwise direction. Therefore it is said that during light propagation along the optic axis of optically active crystals there occurs a *rotation of the polarization plane*; if $G_{33} > 0$, the rotation is right-handed, if $G_{33} < 0$, it is left-handed. It must be borne in mind, however, that within the crystal not at all a linearly polarized wave with a gradually rotating direction of polarization propagates, but two circularly polarized waves travelling with different velocities; only due to the interference of these waves upon leaving the crystal there develops a new linearly polarized wave whose direction of polarization makes up angle ψ with the direction of polarization of the wave incident on the crystal.

The optical activity of crystals is often characterized by the quantity of *specific rotation*, i.e. by the rotation of the polarization plane across a path of 1 mm.

The optical activity of crystals, and, in particular the quantity, of specific rotation is essentially dependent on the frequency of light; this phenomenon is called the dispersion of optical activity. If a linearly polarized white light is directed against a plate which rotates the polarization plane, any monochromatic component of the light leaving the plate will be linearly polarized, but the position of the polarization plane will change with the wavelength. Without an analyzer such light will be perceived as white light, but if transmitted through an analyzer it will appear coloured, the colouring changing with the rotation of the analyzer.

In the intervals of the crystal's transparency the quantity of specific rotation α increases with the increase of the frequency of light ω approximately as ω^2, the gyration tensor **G** increases approximately as ω, while the tensor of optical activity γ depends on the frequency but little. The frequency dependence of these quantities for a quartz crystal (class 32) is given in Table 81.2 (λ_0 is the wave-

Table 81.2

Dispersion of Specific Rotation α, of Components of Pseudo-tensor of Gyration G_{33}, of Tensor of Optical Activity λ_{123}; and of Parameter $G_{33}\lambda/a$ in a Quartz Crystal

λ_0, nm	α, deg/mm	G_{33}, 10^{-5}	γ_{123}, pm	$G_{33}\lambda/a$	λ_0, nm	α, deg/mm	G_{33}, 10^{-5}	γ_{123}, pm	$G_{33}\lambda/a$
686.7	15.55	1.62	1.15	0.0134	486.1	32.69	2.37	1.185	0.0138
656.3	17.22	1.71	1.16	0.0135	430.8	42.37	2.70	1.19	0.0139
589.3	21.67	1.93	1.17	0.0136	396.9	50.98	2.97	1.20	0.0141
527.0	27.46	2.17	1.18	0.0137					

length of light in a vacuum). It can be seen that the optical activity of the crystal as such is most conveniently characterized by tensor γ. A dimensionless parameter $G_{33}\lambda/a$ can also be used for this purpose, a being the lattice constant in the direction of the light propagation.

If the perpendicular to the plate makes up a sufficiently large angle with the crystal's optic axis, the change of the character of polarization of light traversing such a plate will be essentially different from the one described above. The optical activity now has the form of elliptic birefringence. Let us use the coordinate system introduced at the beginning of this Section: axis X_3 coincides with the direction of light propagation, and axes X_1 and X_2, with the principal axes of the optical indicatrix central section by the wave-front plane, axis X_1 coincides with the major axis, axis X_2, with the minor axis ($n_{01} > n_{02}$).

Let us consider a simple example: linearly polarized light with vibration direction $\boldsymbol{e}_1$ is incident on an elliptically birefringent plate. In the absence of optical activity ($G_{33} = 0$) the light would retain its polarization both inside the plate and on leaving it. Therefore all alterations of the character of polarization of such light after passing across the elliptically birefringent crystal plate are caused exclusively by the optical activity of the crystal.

Upon entering the crystal a linearly polarized wave breaks up into two elliptically polarized waves, as shown in Fig. 81.1*a*. The arrows show the circuit direction along the ellipses (when $G_{33} > 0$), and the points on the ellipses mark the positions of the ends of vectors $\boldsymbol{D}$ of the two waves at a certain moment. The ellipticity $\rho \approx G_{33}/(n_{02}^{-2} - n_{01}^{-2})$ in the picture is greatly exaggerated. A straight line intercept (the bold line) is the sum of the two vibrations; these are, as it should be, simply the linearly polarized vibrations directed along axis X_1.

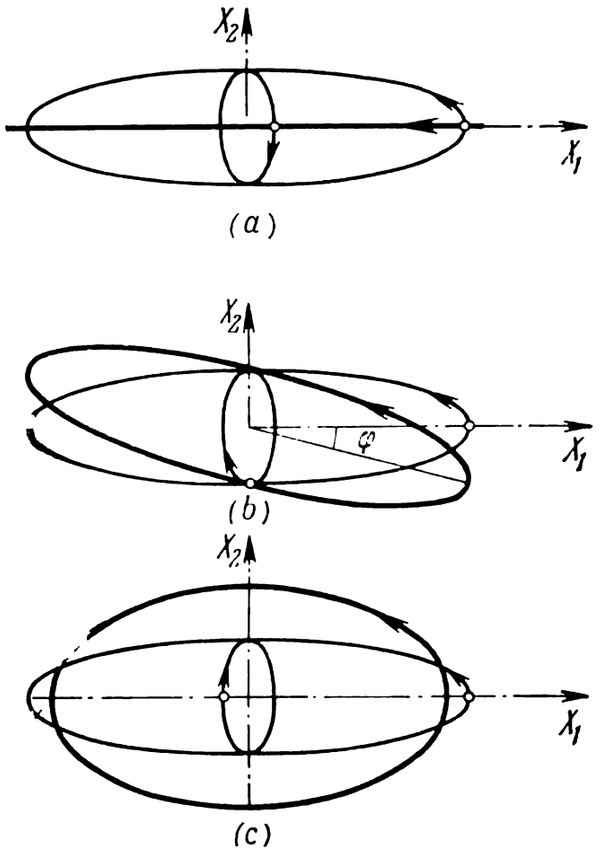


Fig. 81.1. The interference of the elliptically polarized waves propagating in an optically active crystal: (a) decomposition of a linearly polarized wave with the vibrations direction X_1 into two elliptically polarized waves at its entrance into the crystal; (b) the result of the interference of these waves upon their passing across the plate in quarter-wave; (c) the result of their interference upon passing across the plate in a half-wave. The ellipticity is greatly exaggerated for better lucidity. The directions of the circuit along the ellipses are shown for $G_{33} > 0$

Having traversed the plate with different velocities, the waves acquire a certain path difference. Since $n_1 > n_2$, the wave described by the smaller ellipse will have a phase lead with respect to the wave described by the larger ellipse. In particular, if the plate thickness

$$d = \frac{\lambda_0}{n_1 - n_2}\left(\frac{1}{4} + m\right) \approx$$
$$\approx \frac{\lambda_0}{n_{01} - n_{02}}\left(\frac{1}{4} + m\right),$$

where m is any integer (such a plate is called a "quarter-wave plate"), the less intense wave will be a quarter of a revolution ahead of the more intense one. This is shown in Fig. 81.1*b*. Adding the two vibrations together we shall see that due to interference an elliptically polarized light will leave the crystal; its ellipticity is approximately equal to ρ and the major axis of the vibration ellipse, shown in

bold type in the picture, is turned clockwise with respect to the vibration direction of the incident light by the angle $\varphi \approx \rho$.

For a plate of thickness

$$d = \frac{\lambda_0}{n_1 - n_2}\left(\frac{1}{2} + m\right)$$

("half-wave plate") the phase difference will be π. The light leaving the plate is elliptically polarized, its vibrations are shown in the picture by a bold ellipse (Fig. 81.1*c*); its ellipticity is approximately equal to 2ρ, and the major axis coincides with the vibration direction of the incident light.

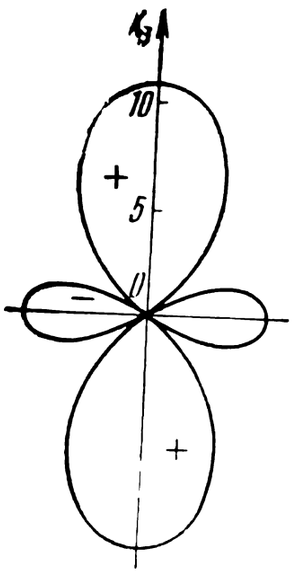


Fig. 81.2. The representation surface of a pseudotensor of gyration for the right-hand α-quartz, class 32. The plus sign means rotation to the right, the minus sign to the left, in 10^{-5}

These effects are very small because of the smallness of the parameter ρ characterizing their magnitude, but with sufficiently good instruments they can be registered; the optical activity of crystals is measured not only along the optic axes, but also in the directions in which birefringence is essentially marked (Konstantinova, Ivanov, Grechushnikov, 1969; Ivanov and Konstantinova, 1970). In the result it is possible to obtain the representation surface of the pseudotensor of gyration (see, e.g. Fig. 81.2).

The optical activity of crystals is characterized by a second-rank pseudotensor **G**. Since it is of an odd type, optical activity can be displayed only by crystals of non-centrosymmetric classes. In a general case the pseudotensor is not symmetric and can be decomposed into a symmetric (G^s) and antisymmetric (G^a) parts (see Sec. 18). Their importance for the optical activity of crystals is by far not equivalent. Equations (81.10) that determine the character of polarization of light waves in optically active crystals, contain the component G_{33} of the pseudotensor of gyration referred to the special system of coordinates in which the axis X_3 is directed along the vector of the wave normal $\boldsymbol{n}$. In an arbitrary (in particular, in the crystal physical) frame of coordinates this quantity is equal to $\boldsymbol{n}\cdot\mathbf{G}\cdot\boldsymbol{n}$— to the normal component of pseudotensor **G** in the direction **n**. This component is fully determined by the symmetric part $\mathbf{G}^s$. Therefore, investigating the polarization of waves in a crystal the pseudotensor of gyration can be regarded as symmetric.

Table E.7 shows the form of pseudotensor $\mathbf{G}^s$ for all crystallographic classes. In the crystallographic system of coordinates it has 9 different forms. But this does not at all mean that there are 9 symmetry classes of optical activity: upon referring the pseudotensors,

given in Table E.7, to the principal axes,* we shall see that there are only four such classes. They are listed in Table 81.3.

The tensor of gyration depends on frequency. This phenomenon is called the *dispersion of optical activity*. Changes of the tensor of gyration caused by dispersion can result in the rotation of its eigenvectors and, consequently, in the change of the tensor's orientation with respect to the crystal. Exactly the difference between the number of the independent components of the pseudotensor of gyration and the number of parameters characterizing the optical activity shows the number of quantities specifying the orientation of the pseudotensor of gyration with respect to the crystal of the given class.

To one and the same symmetry class of optical activity can correspond several classes of the symmetry of its dispersion. Thus, when the symmetry of optical activity is 222, the symmetry of its dispersion can be either 222, or 2, or 1. We have already met a similar situation in the investigation of the symmetry of dielectric properties of crystals. When the symmetry of optical activity is $\bar{4}2\,m$, three symmetry classes of its dispersion are also distinguished; in crystals of classes $\bar{4}2m$ and $mm2$ the eigenvectors are rigidly connected with the symmetry elements of the crystal; in crystals of class $\bar{4}$ only one of the eigenvectors is fixed—the vector corresponding to the zero eigenvalue; finally, in crystals of class m the eigenvector corresponding to the zero eigenvalue can rotate with the change of frequency, remaining all the time in the symmetry plane of the crystal, while the other two eigenvectors rotate together with it so that each of them is always inclined at the angle of 45° to the symmetry plane. There are all in all 8 symmetry classes of the dispersion of optical activity; they are also listed in Table 81.3.

Optical activity manifests itself in the elliptic or circular birefringence: monochromatic light passing across a crystal breaks up into two elliptically or circularly polarized waves of opposite orientation propagating at different velocities. This phenomenon calls for a non-zero component of the pseudotensor of gyration directed along the wave normal $\boldsymbol{m}\cdot\mathbf{G}\cdot\boldsymbol{m}$ but in Sec. 44 it was shown that such components can differ from zero only in screw directions (see Fig. 44.1, *d*). A direction can be a screw one in that and only that case when the crystal's symmetry group does not contain a single operation which would transform this direction into itself, and would

* A symmetric second-rank pseudotensor is reduced to its principal axes exactly in the same way as a symmetric second-rank tensor, only its own eigenvalues are not scalars but pseudoscalars. Therefore care should be taken in the choice of the direction and enumeration of eigenvectors so as not to replace the right-hand triplet of mutually orthogonal unit vectors by a left-hand one, or vice versa: if the replacement was done, all eigenvalues are to be multiplied by -1.

Table 81.3

Symmetry of Optical Activity and Its Dispersion

Eigenvalues of the pseudotensor of gyration	$K(G^{(s)})$	m	$K^{(\omega)}(G^{(s)})$	n	Crystallographic and limit classes contained in the given class of dispersion of optical activity
$G_{(1)} \neq G_{(2)} \neq G_{(3)}$	222	3	1	6	1
			2	4	2
			222	3	222
$G_{(1)} = -G_{(2)}$ $G_{(3)} = 0$	$42m$	1	m	2	m
			4	2	$\bar{4}$
			$\bar{4}2m$	1	$mm2$, $\bar{4}2m$
$G_{(1)} = G_{(2)} = G_{(3)}$	$\infty 2$	2	$\infty 2$	2	3, 32, 4, 422, 6, 622, ∞, $\infty 2$
$G_{(1)} = G_{(2)} = G_{(3)}$	$\infty\infty$	1	$\infty\infty$	2	23, 432, $\infty\infty$

Notation. $K(G^{(s)})$ is the symmetry class of optical activity. $K^{(\omega)}(G^{(s)})$ is the symmetry class of the dispersion of optical activity. m is the number of the parameters characterizing optical activity. n is the number of independent components of the symmetric pseudotensor of gyration.

simultaneously transform a right-hand screw into a left-hand one. Thus, the symmetry group must not contain inversion, reflection in a plane perpendicular to the given direction, any inversion (or mirror) rotation about an axis coinciding with the given direction, and finally, reflection in any of the planes containing the given direction. Non-screw and especially screw directions for crystals of all classes are given in Table C.1. If the symmetry operations of a crystal contain inversion, i.e. if the crystal is centrosymmetric no direction in this crystal can be a screw one, and consequently the crystal cannot be optically active.

If among operations of the crystal there are none of the second kind, i.e. the crystal is enantiomorphous, any direction in it is a screw one. The elliptic or circular birefringence in any direction* is pos-

* This does not mean, however, that it certainly occurs in all directions. In quartz, for example, normal components of the pseudotensor of gyration in the direction of the principal symmetry axis and in the directions perpendicular to it have different signs. Hence the availability of the cone of directions

sible only in such substances. In principle all enantiomorphous substances can exist in two modifications: the right- and the left-hand one. Pseudotensors of gyration of the right- and left-hand modifications are mutally opposite: $\mathbf{G}_{\text{left}} = -\mathbf{G}_{\text{right}}$ (tabulated values are usually given for the right-handed modification). Therefore, if in one of the enantiomorphous modifications a right-hand-polarized wave travels at a higher velocity in a certain direction, in the other modification a left-hand-polarized wave will travel with an equally higher velocity in the corresponding direction.

The most pronounced manifestation of optical activity of crystals is the rotation of the polarization plane of light propagating along the optic axis. In gyrotropic media and in enantiomorphous crystals of the cubic system it is possible in any direction, and the specific rotation in all directions is the same (for the light of a given frequency). In enantiomorphous crystals of the intermediate category it is possible in the direction of their sole optic axis. Crystals of the lower category have two optic axes. In class 222 they are symmetrically equivalent, so that the rotation about both axes is of the same direction and through the same angle. In class 1 optic axes are in no way interconnected and their specific rotations are different. As for the crystals of class 2, both the first and the second situation can be realized depending on whether the symmetry axis lies in the optic axes plane or is perpendicularly to it. Actually, both these possibilities are realized: the first—in crystals of tartaric acid, the second, in crystals of sugar and rhamnose.

Now let us turn our attention to non-centrosymmetric crystals and media whose symmetry groups contain operations of the second kind. One of such groups, namely ∞m, forbids the existence of screw rotations, and consequently of optical activity. Indeed, in this case any direction lies in one of the symmetry planes and therefore cannot be a screw direction. Since optical activity is described by a second-rank pseudotensor, Hermann's theorem forbids optical activity also in crystals of classes $3m$, $4mm$, $6mm$, although there are screw directions in these crystals. From Hermann's theorem there also follows the impossibility of optical activity in crystals of classes $\bar{6}$, $\bar{6}m2$ and $\bar{4}3m$: substituting the three-fold axes in these classes by the axes of an infinite order we obtain centrosymmetric limit classes ∞/m, ∞/mm, and $\infty\infty m$ respectively.

Thus, optical activity is permitted only by four classes which have operations of the second kind: m, $mm2$, $\bar{4}$ and $\bar{4}2m$. The directions coinciding with the $\bar{4}$-fold axes or lying in the symmetry planes of these classes are non-screw ones. Actually, all crystals of these

in which this normal component is zero and birefringence is linear (see Fig. 81.2). However, the symmetry of quartz crystals (class 32) does not call for the existence of such directions.

classes have mutually perpendicular planes consisting of directions in which optical activity is not displayed because the symmetry of their gyration tensor is $\bar{4}2\ m$. Any right-handed screw direction in crystals of this type is transformed by the symmetry operations of the second kind into a left-handed screw direction, and vice versa. Therefore, right- and left-handed screw directions in these crystals are available, so to speak, in equal quantities. The rotation of the polarization plane of light propagating along the optic axis is possible only in two classes of this type: m and $mm2$ and only provided

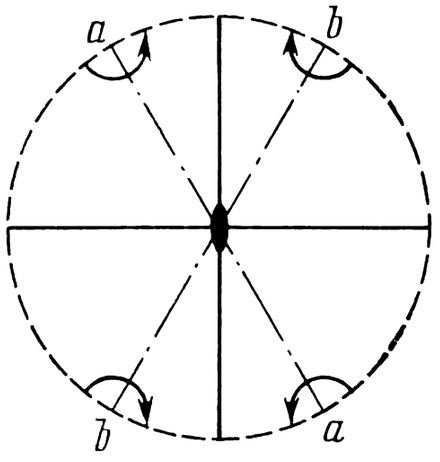


Fig. 81.3. Rotation of the polarization plane of light propagating along the optic axes in a crystal of class $mm2$. Stereographic projection. Dot-and-dash lines denote the optic axes, the circular arrows about them show the direction of rotation of the polarization plane. About axis aa rotation is to the left, about axis bb rotation is to the right and of the same intensity

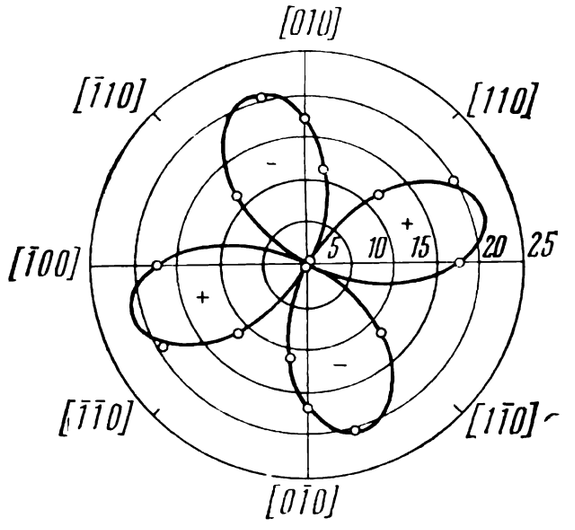


Fig. 81.4. Specific rotation of the polarization plane of a crystal of cadmium thiogallate (class $\bar{4}$) in plane (001); in K/mm (Hobden, 1969). It can be seen that the pseudotensor of gyration has $\bar{4}2m$ symmetry, but its two-fold symmetry axes do not coincide with the crystal-physical axes X_1, i.e. [100] and X_2, i.e. [010]

that the optic axes do not lie in the symmetry planes. In this case the magnitude of rotation along the two optic axes is the same, while its directions are opposite. Fig. 81.3 illustrates this by an example of rotation of the polarization plane in crystals of class $mm2$. It was observed in a crystal of sodium nitrite belonging to this class (Chern, Phillips, 1970) and of sodium zinc-germanate, Na_2ZnGeO_4, class m (Kozyrev, Gilvarg, Grechushnikov, Belov, 1973).

If in a uniaxial crystal of an optically active class the refractive indices N_o and N_e become at a certain wavelength equal to each other, the rotation of the polarization plane of light of this wavelength can occur in any direction permitted by the symmetry of optical activity. Thus, in a crystal of silver thiogallate, $AgGaS_2$ (class

$\bar{4}2m$), birefringence reverses its sign at the wavelength $\lambda = 4974$ Å. At this wavelength Hobden (1968) observed the rotation of the polarization plane; when light propagates along the crystal-physical axes X_1 and X_2 specific rotation has, as it should, opposite signs (see Fig. 44.4). Similar observations were made in crystals of cadmium thiogallate (class $\bar{4}$); their results are shown in Fig. 81.4.

Let us discuss the antisymmetric part of the pseudotensor of gyration $G^{(a)}$. An antisymmetric second-rank pseudotensor is dual of the ordinary polar vector: $\varepsilon\{V^2\} \sim V$; therefore the antisymmetric part of the pseudotensor of gyration can differ from zero only in those crystals whose symmetry permits the existence of a matter vector, i.e. in crystals and textures of the pyroelectric classes

$$1,\ 2,\ 3,\ 4,\ 6,\ \infty,\ m,\ mm2,\ 3m,\ 4mm,\ 6mm,\ \infty m.$$

Among the listed classes which permit optical activity, as it is usually understood there are such classes which do not admit it:

$$3m,\ 4mm,\ 6mm,\ \infty m.$$

We shall call the crystals and textures of such classes *slightly active optically*; Agranovich and Ginsburg (1979) use the term *weakly gyrotropic*. Pseudotensors of gyration in such substances are antisymmetric. The polarization of light propagating in weakly optically active crystals is of a highly peculiar character. The electric induction vectors of all light waves propagating in such crystals are linearly polarized. If there were no optical activity at all, the electric field vector of the light wave would be linearly polarized (although, generally speaking, it would extend beyond the wave-front plane) and the whole wave could be considered linearly polarized. When optical activity is available, the electric field vector is connected with the vector of the electric induction by material equations (81.7) which in the case of weak activity appear as

$$\boldsymbol{E} = \eta\cdot\boldsymbol{D} + im\boldsymbol{h}\cdot\boldsymbol{D}, \tag{81.25}$$

here $\boldsymbol{h}$ is the vector dual of the antisymmetric pseudotensor G:

$$G_{jk} = \delta_{jkl}h_l, \quad h_i = \frac{1}{2}\delta_{ijk}G_{jk}; \tag{81.26}$$

in crystals of the intermediate category it is parallel to the optic axis. For waves propagating along the optic axis and generally for all ordinary waves $\boldsymbol{h}\cdot\boldsymbol{D} = 0$, so that vector $\boldsymbol{E}$ of the ordinary wave is linearly polarized. But when the wave is extraordinary, vector $\boldsymbol{E}$ is elliptically polarized, the ellipse being located in the plane passing through the crystal's optic axis and the wave normal, i.e. in the plane perpendicular to the wave front. This is as it must be: this is the only kind of elliptic polarization possible in a non-screw direction. During each period the field vector $\boldsymbol{E}$ twice

becomes purely longitudinal, though at these moments, it becomes very small ($E_{\text{long}} \sim hE_{\text{ampl}}$) corresponding to the small (of the order h) ellipticity.

It appears that F. I. Fedorov (1959) was the first to notice weak optical activity. It must accompany the reflection and refraction of light, since the boundary conditions call for a continuous tangential component of the intensity vector on the interface.

Problems of the optical activity of crystals are discussed, for instance, in the works of F. I. Fedorov (1959a and 1975); Bokut', Serdyukov and Fedorov (1970); V. N. Alexandrov (1970); Bokut' and Serdyukov (1971); Agranovich and Ginsburg (1972).

Sec. 82. Artificial Optical Activity

By an artificial (induced) optical activity is meant the appearance or alteration of optical activity under the external influences; an electric or magnetic field, mechanical stresses, and so on. Recently there was observed a foretold (Zheludev, 1964) influence of an electric field on the optical activity of crystals—the *electrogyrational effect* (Blokh, 1971)*: with the electric field vector $\boldsymbol{E}$ the pseudotensor of crystal gyration is equal to

$$G_{ij}(E) = G_{ij}^{(0)} + A_{ijk}E_k + B_{ijkl}E_kE_l. \tag{82.1}$$

The internal symmetry of pseudotensor **A** is $\varepsilon\,[V^2]\,V$ (the weak optical activity being neglected). This is an even-type tensor; its form is shown in Table E.14 and for any subsystem it coincides with the form of tensor $V\,[V^2]$ for the enantiomorphous class of this subsystem (cf. Table E.11). Although even-type tensors usually do not vanish, this tensor does so for two subsystems: $\infty\infty m$ and $m3m$. Thus the linear electrogyrational effect is impossible in isotropic bodies. Among the classes in which this effect is possible, there are many such classes for which optical activity is forbidden; apparently they are especially convenient for the observation of the above effect.

Pseudotensor **B** with internal symmetry $\varepsilon\,[V^2]^2$ is of the odd type, therefore the quadratic electrogyration in centrosymmetric crystals is impossible. A tensor of the same form describes the influence of mechanical stresses (apparently not yet observed) on optical activity (Ranganath, Ramaseshnan, 1969).

Artificial optical activity under the influence of a magnetic field is, contrary to the above, possible also in isotropic bodies and has long been known. Back in 1846 Faraday discovered that if linearly polarized light is incident in the direction of magnetic lines onto

* Shuvalov and Ivanov (1964), pointed to a similar effect in some ferroelectrics—to the alteration of the sign of optical activity under the repolarization of a crystal.

an isotropic, optically inactive transparent body located in a homogeneous magnetic field, then the light leaving this body will also be linearly polarized, but its polarization plane will be rotated with respect to polarization plane of the incident light by an angle proportional to the path of light in the substance and to the magnetic field.

Faraday's optical activity is explained by the fact that in a magnetic field the tensor of the dielectric impermeability of crystals (and isotropic bodies) becomes somewhat changed. From thermodynamics of irreversible processes it follows that magnetic field intensity $\boldsymbol{H}$ causes the appearance of a complex increment $\Delta\boldsymbol{\eta} = \zeta + i\xi$ to the tensor of dielectric impermeability $\boldsymbol{\eta}$, this increment satisfying relation $\Delta\eta_{jk}(\boldsymbol{H}) = \Delta\eta_{kj}(-\boldsymbol{H})$, or

$$\zeta_{jk}(\boldsymbol{H}) = \zeta_{kj}(-\boldsymbol{H}), \quad \xi_{jk}(\boldsymbol{H}) = \xi_{kj}(-\boldsymbol{H}). \tag{82.2}$$

On the other hand, in transparent crystals this increment (just as the whole tensor $\boldsymbol{\eta}$) is Hermitian, i.e. its real part is symmetric, while the imaginary one is antisymmetric:

$$\zeta_{jk}(\boldsymbol{H}) = \zeta_{kj}(\boldsymbol{H}), \quad \xi_{jk}(\boldsymbol{H}) = -\xi_{kj}(\boldsymbol{H}). \tag{82.3}$$

Having compared conditions (82.2) and (82.3) we shall find that ζ are even and ξ odd functions of the magnetic field intensity. In the first approximation

$$\zeta_{jk} = C_{jklm}H_lH_m; \quad \boldsymbol{\zeta} = \mathbf{C} : \boldsymbol{HH}; \tag{82.4}$$

$$\xi_{jk} = f_{jkl}H_l, \qquad \boldsymbol{\xi} = \mathbf{f}\cdot\boldsymbol{H}. \tag{82.5}$$

Tensors $\mathbf{G}$ and $\mathbf{f}$ satisfy relations[1]

$$C_{iklm} = C_{kjlm} = C_{jkml} = C_{kjml}, \tag{82.6}$$

$$f_{jkl} = -f_{kjl}. \tag{82.7}$$

Evidently, most essential is the effect connected with an increment $i\mathbf{f}\cdot\boldsymbol{H}$, linear with respect to $\boldsymbol{H}$, to the tensor of dielectric impermeability $\boldsymbol{\eta}$.

Let us utilize the duality relations and substitute the pseudotensor $\mathbf{f}$, antisymmetric with respect to two indices by a second-rank tensor $\mathbf{F}$:

$$F_{il} = \frac{1}{2}\delta_{ijk}f_{jkl}, \quad f_{jkl} = f_{jkm}F_{ml}. \tag{82.8}$$

Then, instead of (82.5), we shall have

$$\xi_{jk} = \delta_{ikl}F_{lm}H_m, \quad \boldsymbol{\xi} = \mathbf{I}\times\mathbf{F}\cdot\boldsymbol{H}, \tag{82.9}$$

so that the components of the tensor of dielectric impermeability, altered by the magnetic field, are equal to $\boldsymbol{\eta} + i\mathbf{I}\times\mathbf{F}\cdot\boldsymbol{H}$, if only those terms of the expansion are taken into consideration which are linear with respect to $\boldsymbol{H}$, while the relation connecting the strength

and induction of the electric field of a light wave passing across a crystal located in a magnetic field becomes

$$E_j = (\eta_{jk} + i\delta_{jkl}F_{lm}H_m)\,D_k, \quad \boldsymbol{E} = \eta\cdot\boldsymbol{D} + i\boldsymbol{D} \times \mathbf{F}\cdot\boldsymbol{H}. \qquad (82.10)$$

It is very much like the matter equation of an optically active medium (81.7) and would fully coincide with it in case of identification of axial vectors $\mathbf{F}\cdot\boldsymbol{H}$ and $\mathbf{G}\cdot\boldsymbol{m}$. Pseudoscalar $\boldsymbol{m}\cdot\mathbf{F}\cdot\boldsymbol{H}$ corresponds to the quantity $\boldsymbol{m}\cdot\mathbf{G}\cdot\boldsymbol{m}$ which characterizes optical activity in the direction $\boldsymbol{m}$ quantitatively.

Thus, a transparent medium, whether isotropic or anisotropic, becomes optically active in a magnetic field: light waves propagating in it are elliptically or circularly polarized. This is what is called the *Faraday effect*. Generally it is very weak—usually much weaker than the natural optical activity, and therefore can be observed only in an optically isotropic medium or in case of the propagation of light along the optic axis of the crystal. The artificial optical activity caused by a magnetic field is manifested in the rotation of the polarization plane: the polarization plane of linearly polarized light, which passed through a layer of thickness d, rotates away from its original position by the angle

$$\psi = \frac{n\pi_0^3 d}{\lambda_0} F_{il} m_i H_l = \frac{\pi n_0^3 d}{\lambda_0} \boldsymbol{m}\cdot\mathbf{F}\cdot\boldsymbol{H} \qquad (82.11)$$

in the clockwise direction. Here n_0 is the refractive index of the wave propagating along the optic axis, λ_0 is the wavelength of light in a vacuum, $\boldsymbol{m}$ is the unit vector of the wave normal, $\mathbf{F}$ is the *tensor of Faraday's coefficients*, $\boldsymbol{H}$ is the magnetic field strength.

If the medium is optically isotropic, $F_{il} = F\delta_{il}$, and Faraday's rotation of the polarization plane is characterized by the *Verdet constant* $V = \pi n_0^3 F/\lambda_0$; in non-magnetic substances (glass, water, carbon disulphide) it is of the order of one angular second per oersted by centimetre. In magnetic materials the effect is considerably stronger; it is then proportional not to the magnetic field intensity but to the magnetization of the material.

In the first approximation the magnetic field has no effect on the light propagating in the direction $\boldsymbol{m}$ perpendicular to the axial vector $\mathbf{F}\cdot\boldsymbol{H}$; in this case it is necessary to take into account increments, quadratic with respect to $\boldsymbol{H}$, to the components of the tensor of dielectric impermeability determined by (82.4). Tensor $\zeta = \mathbf{C}\cdot\boldsymbol{HH}$ is real and symmetric; it specifies artificial birefringence: in its pure form, if the direction of light propagation coincides with the optic axis of the crystal, and against the background of a much stronger natural birefringence in the opposite case. This is the *Cotton-Mouton effect* which is perfectly similar to but much weaker

than* the Kerr effect discussed in Sec. 77. **C** is the *Cotton-Mouton tensor* with internal symmetry $[V^2]^2$.

The ability of a substance to acquire optical activity in a magnetic field is characterized by the matter tensor **F**. Since this property also belongs to centrosymmetric (in particular, to isotropic) substances not possessing magnetic structure, the Faraday tensor **F** is of an even type. Hence $\mathbf{F}\cdot\boldsymbol{H}$ is a vector of a magnetic type, i.e. an axial vector reversing its direction with time inversion. Since the vector of the wave normal $\boldsymbol{m}$ also reverses its direction with time inversion, $\boldsymbol{m}\cdot\mathbf{F}\cdot\boldsymbol{H}$ becomes, just as $\boldsymbol{m}\cdot\mathbf{G}\cdot\boldsymbol{m}$, a pseudoscalar of the electric type, i.e. with symmetry $\infty\infty 1'$ (see Sec. 68)**.

With respect to symmetry there is an essential difference between Faraday's optical activity and the natural one. While natural optical activity occurs only in screw directions, Faraday's activity is possible also in non-screw directions. Actually, a centrosymmetric body remains the same in a magnetic field, since the latter is also centrosymmetric; thus it has no screw directions, but nevertheless the rotation of the polarization plane occurs. In crystals and isotropic bodies placed in a magnetic field all those directions are axial (see Secs 14, 44 and Appendix C) for which the normal component of the axial vector $\mathbf{F}\cdot\boldsymbol{H}$ differs from zero. In such directions there are distinguished the velocities not of the right- and left-hand polarized waves, but of the waves in which the direction of the circuit along the circle or ellipse of polarization coincides with the direction of the axial vector or is opposite to it. Thus, in case of natural optical activity, electrogyration and hypothetical piezogyration the circular (elliptic) birefringence is of the *screw* type, while in case of Faraday's effect in optically inactive media it is *axial*. The distinction between these two types becomes highly pronounced if the light transmitted across an active medium is reflected in a mirror and directed back along the path it has just passed. Upon reflection the screw orientation of light is reversed (the right-hand-polarized light becomes left-hand-polarized), while axial orientation remains unchanged. Therefore, when circular or elliptic birefringence is of the screw type, the path difference, acquired by the two waves in their forward travel, is lost by them in the return travel; on the contrary, when birefringence is of the axial type, the path difference continues to increase during the return travel of light, which allows using multiple reflections for the amplification of the effect.

However, the term "axial" cannot be understood literally. If only the axiality of direction mattered, the circular birefringence of the axial type would be observed in case of the propagation of light along the optic axes of crystals of central classes of the inter-

* With the exception of transparent ferro- and antiferromagnetic crystals (see Smolensky, Pisarev, Sinyi, Kolpakova, Titova, 1972).

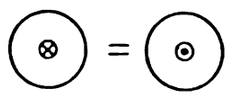
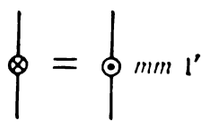
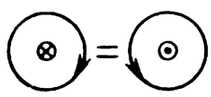
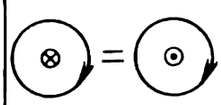
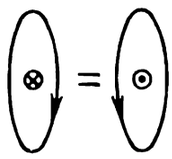
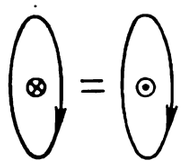
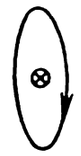
** For more details on Faraday's tensor see Ranganath (1972).

mediate category ($\bar{3}$, $4/m$, $6/m$) in the absence of a magnetic field, but it is not observed under these conditions. From the explanation of the Faraday effect it is apparent that only magnetic axial directions, i.e. directions with a symmetry not higher than ∞/mm' can serve as the directions of circular or elliptic birefringence of axial type. Such a dissymmetry of direction is possible not only in a non-magnetic medium under the action of an external magnetic field, but also in ferromagnetic crystals (see Sec. 70). For this Faraday's (axial) optical activity will henceforth be discussed irrespective of its being artificial or natural. Although the explanation of the natural Faraday's optical activity of ferromagnetic crystals (see Krinchik and Chetkin, 1969) differs somewhat from the above explanation of Faraday's effect, the symmetry in both cases is the same.

All logically possible cases of optical properties of directions are collected in Table 82.1. Along with already known directions of circular birefringence of

Table 82.1

Optical Properties of Directions, Their Graphic Representation and Symmetry

What light can propagate in a given direction	Upon reversal of direction of propagation light velocity		
	remains unchanged		changes
	for light of a given screw orientation	for light of a given axial orientation	
natural	 $\infty/mm1'$		$\infty/m'm$
linearly polarized	 $mm1'$		mmm'
circularly polarized	 $\infty 21'$	 ∞/mm'	$\infty 2'$
elliptically polarized	 $2221'$	 $m'm'm$	 $2'2'2$

the screw (symmetry $\infty\ 21'$) and axial (∞/mm') types, the Table presents still another type of direction in which there is neither screw nor axial circular birefringence, but light travels forward and backward with different velocities. The operations contained in its symmetry group $\infty/m'm$ transform the right-hand screw into the left-hand one and one axial orientation into another not changing the direction of propagation. The dissymmetry necessary for linear birefringence was discussed in Sec. 25 (there it was called simply birefringence). A combination of dissymmetries necessary both for the linear and circular birefringence of one or the other type results in elliptic birefringence of a corresponding type. Table 82.1 makes it possible to determine optical properties of any direction in any crystal. For this purpose it is necessary to find the magnetic symmetry group for the given direction

$$G_{\text{dir}} = G \cap \infty/mm1' \qquad (82.12)$$

where G is the magnetic symmetry group of the crystal, and its axis ∞ is parallel to the direction we are concerned with. If the crystal experiences external influences—uniaxial stress, an electric or magnetic field—then in relation (82.12) G should be replaced by

$$G_{\text{cr.infl}} = G \cap G_{\text{infl}} \qquad (82.13)$$

where G_{infl} is the magnetic symmetry group of influence: $\infty/mm1'$, $\infty m1'$, or ∞/mm' respectively. Then it is necessary to determine which of the ten magnetic symmetry groups G_{opt}, given in Table 82.1, are the supergroups of the symmetry group of direction found by means of formula (82.12)

$$G_{\text{opt}} \supseteq G_{\text{dir}} \qquad (82.14)$$

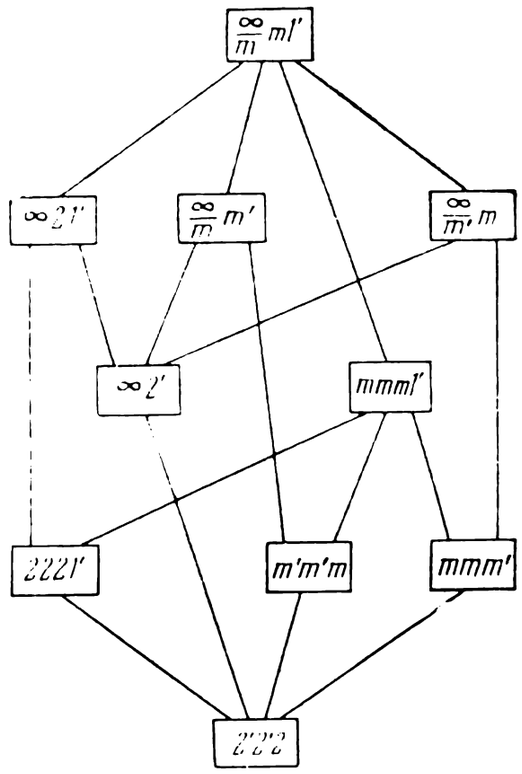


Fig. 82.1. Schematic diagram of mutual subordination of the symmetry groups of the optical properties of directions

and to find the lowest one among them; it will be the one that determines the symmetry of the optical properties of the given direction. For this purpose Fig. 82.1 can be used: it gives the diagram of mutual subordination of these groups. The ban of an effect is absolute, as usually, but the effect being permitted does not mean that it actually takes place. In any case, transparent magnetically ordered crystals can be expected to have highly peculiar optical properties; some of them are foretold by the above Table, but evidently have not been observed yet.

Sec. 83. Acoustic Activity of Crystals

The influence of spatial dispersion on the propagation of elastic waves in non-centrosymmetric crystals and gyrotropic bodies causes *acoustic activity*—the acoustic analogue of optical activity (Andronov, 1960). When spatial dispersion is taken into consideration, the generalized Hooke's law (51.3) in the first approximation has the following form

$$\sigma_{ij} = c_{jkl}\varepsilon_{kl} + b_{ijkln}\frac{\partial \varepsilon_{kl}}{\partial x_n}. \qquad (83.1)$$

The *tensor of acoustic gyration* **b** which characterizes the spatial dispersion of elastic properties of crystals, is symmetric as well as **c**, with respect to the first (ij) and the second (kl) pair of indices; this permits rewriting (83.1) as

$$\sigma_{ij} = c_{ijkl} \frac{\partial u_k}{\partial x_l} + b_{ijkln} \frac{\partial^2 u_k}{\partial x_l \, \partial x_n} \tag{83.2}$$

(cf. the transition from (51.3) to (51.13)). Hence we find the change of the equations of elastodynamics (51.14) caused by the allowance made for the spatial dispersion:

$$c_{ijkl} \frac{\partial^2 u_k}{\partial x_i \, \partial x_l} - b_{ijkln} \frac{\partial^3 u_k}{\partial x_i \, \partial x_l \, \partial x_n} = \rho \frac{\partial^2 u_j}{\partial t^2} . \tag{83.3}$$

For plane waves $\boldsymbol{u} = A\boldsymbol{p} \exp [(2\pi i/\lambda) (\boldsymbol{m} \cdot \boldsymbol{r} - vt)]$ equations (83.3) have the following form:

$$\begin{gathered} [c_{ijkl} m_i m_l + (2\pi i/\lambda) \, b_{ijkln} m_i m_l m_n] \, p_k = \rho v^2 p_j, \\ [\boldsymbol{m} \cdot \mathbf{c} \cdot \boldsymbol{m} + (2\pi i/\lambda) \, \boldsymbol{m} \cdot \mathbf{b} : \boldsymbol{mm}] \cdot \boldsymbol{p} = \rho v^2 \boldsymbol{p}. \end{gathered} \tag{83.4}$$

These are Christoffel equations for acoustically active crystals. They show that in crystal acoustics, like in the theory of optical activity, spatial dispersion results in the appearance of a pure imaginary increment to tensor **c**, and the absence of absorption means that the complex tensor $c_{\lambda\mu} + (2\pi i/\lambda) \, b_{\lambda\mu n} m_n$ is Hermitian, so that its imaginary part is antisymmetric: $b_{\lambda\mu n} = -b_{\mu\lambda n}$. Thus, the internal symmetry of tensor **b** is $\{[V^2]^2\} \, V$. Since tensor **b** is contained in basic equation (83.4) in the form of $\boldsymbol{m} \cdot \mathbf{b} : \boldsymbol{mm}$, its most essential part is the one symmetric with respect to the first, fourth and fifth indices—the *symmetrized tensor of acoustic gyration.* For this tensor the antisymmetry with respect to permutation of the first and second pairs of indices reduces to antisymmetry with respect to the second and third indices, so that its internal symmetry is equal to $\{V^2\} \, [V^3]$. This allows, with the aid of the duality relation $\{V^2\} \, [V^3] \sim \sim \varepsilon V \, [V^3]$, to introduce the *pseudotensor of acoustical gyration* **g**:

$$\begin{gathered} g_{siln} = \frac{\pi}{\lambda} \delta_{sjk} b_{ijkln} , \\ \frac{2\pi}{\lambda} b_{ijkln} = \delta_{jks} g_{siln}. \end{gathered} \tag{83.5}$$

By means of pseudotensor **g** the *axial vector of acoustical gyration* which depends on the direction of the wave normal $\boldsymbol{m}$ is defined:

$$\boldsymbol{Q} = \mathbf{g} \vdots \boldsymbol{mmm}, \qquad Q_s = g_{siln} m_i m_l m_n. \tag{83.6}$$

Together with Christoffel tensor $\mathbf{M} = \boldsymbol{m} \cdot \mathbf{c} \cdot \boldsymbol{m}$, introduced in Sec. 56, it allows to bring Christoffel equations (83.4) to their final form:

$$\begin{gathered} (M_{jk} + i\delta_{jkl} Q_l) \, p_k = \rho v^2 p_j, \\ \mathbf{M} \cdot \boldsymbol{p} + i\boldsymbol{p} \times \boldsymbol{Q} = \rho v^2 \boldsymbol{p}. \end{gathered} \tag{83.7}$$

Thus, the pseudotensor of acoustic gyration **g** with internal symmetry $\varepsilon V \, [V^3]$ is what mainly determines the acoustic activity of crystals. In a general case (i.e. for crystals of class 1) it has 30 independent components, while tensor **b** with symmetry $\{[V^2]^2\} \, V$ which exhaustively describes the acoustical activity, has 45 independent components.

Matter pseudotensors $\varepsilon V \, [V^3]$ are not given in Appendix E*. The form of these pseudotensors for all non-centrosymmetric crystallographic classes can be

* For crystallographic groups consisting only of operations of the first kind the form of pseudotensors $\varepsilon V \, [V^3]$ coincides with the form of tensors $V \, [V^3]$ given in Table E.17. The general pseudotensor of the fourth rank was discussed by Barkovsky (1970).

obtained by expanding the tensors into irreducible parts (see Sec. 52); this method is based on the theory of group representation. We shall represent pseudotensor **g** as

$$\mathbf{g}=\mathbf{g}^{\{4\}}+\mathbf{g}^{\{31\}};$$
$$g^{\{4\}}_{ijkl}=g_{(ijkl)}, \qquad g^{\{31\}}_{ijkl}=g_{ijkl}-g_{(ijkl)}; \tag{83.8}$$

thus, pseudotensor $\mathbf{g}^{\{4\}}$ is symmetric with respect to all indices, $\mathbf{g}^{\{31\}}$only with respect to the last three indices while under symmetrization with respect to all indices it vanishes.

It can be shown (the theory of group representation being required for this very point) that pseudotensor $\mathbf{g}^{\{4\}}$ consists of parts transforming as a pseudoscalar $\tilde{I}$, a pseudodeviator $\tilde{\mathbf{D}}$ and a pseudononor $\tilde{\mathbf{N}}$, while $\mathbf{g}^{\{31\}}$ consists of parts transforming as vector V, pseudodeviator $\tilde{\mathbf{D}}$ and septor **S**. Tensors of such internal symmetry as $\mathbf{g}^{\{4\}}$ and $\mathbf{g}^{\{31\}}$ are composed from these quantities uniquely up to numerical coefficients, namely

$$g_{ijkl}=\tilde{I}^{\{4\}}\delta_{(ij}\delta_{kl)}+\tilde{D}^{\{4\}}_{(ij}\delta_{kl)}+\tilde{N}^{\{4\}}_{ijkl}+$$
$$+\delta_{ni(j}\delta_{kl)}V^{\{31\}}_{n}+(\tilde{D}^{\{31\}}_{i(j}\delta_{kl)}-\tilde{D}^{\{31\}}_{(ij}\delta_{kl))}+\delta_{ni(j}S^{\{31\}}_{kl)\,n}. \tag{83.9}$$

The superscripts show to what tensor, $\mathbf{g}^{\{4\}}$ or $\mathbf{g}^{\{31\}}$, the given term of the expansion belongs. Substituting into this expansion general forms of irreducible tensors, invariant with respect to crystallographic groups (see Table 47.3), we obtain the general form of pseudotensors **g** for the corresponding groups.

Substituting expansion (83.9) into (83.6) we find a general formula for the axial vector of acoustical gyration

$$Q_i=\tilde{I}^{\{4\}}m_i+\delta_{ijn}m_jV^{\{31\}}_n+\frac{1}{2}(\tilde{D}^{\{4\}}_{ij}+\tilde{D}^{\{31\}}_{ij})\,m_j+$$
$$+\frac{1}{2}(\tilde{D}^{\{4\}}_{kl}-\tilde{D}^{\{31\}}_{kl})\,m_im_km_l+\delta_{ijn}S^{\{31\}}_{kln}m_jm_km_l+\tilde{N}^{\{4\}}_{ijkl}m_jm_km_l, \tag{83.10}$$

$$\boldsymbol{Q}=\tilde{I}^{\{4\}}\boldsymbol{m}+\boldsymbol{m}\times\boldsymbol{V}^{\{31\}}+\frac{1}{2}(\tilde{\mathbf{D}}^{\{4\}}+\tilde{\mathbf{D}}^{\{31\}})\cdot\boldsymbol{m}+$$
$$+\frac{1}{2}\,[\boldsymbol{m}\cdot(\tilde{\mathbf{D}}^{\{4\}}-\tilde{\mathbf{D}}^{\{31\}})\cdot\boldsymbol{m}]\,\boldsymbol{m}+\boldsymbol{m}\times\mathbf{S}^{\{31\}}:\boldsymbol{mm}+\tilde{\mathbf{N}}^{\{4\}}\vdots\,\boldsymbol{mmm}.$$

By means of formula (83.10) it is possible to find vector $\boldsymbol{Q}$ and to write the Christoffel set of equations (83.7) for any non-centrosymmetric crystallographic class and for any direction of the wave normal $\boldsymbol{m}$. Solving this set of equations we shall assume that a corresponding problem of crystal acoustics has already been solved, without allowance made for the acoustical activity, i.e. that we know the velocities v_{0l} and real vectors of polarization $\boldsymbol{p}^{(0l)}$ of elastic waves satisfying equations $\boldsymbol{M}\cdot\boldsymbol{p}=\rho v^2\boldsymbol{p}$ and we shall now learn how they change under the influence of the acoustical activity of the crystal.

Let us first consider the case when the wave normal $\boldsymbol{m}$ is not the crystal's acoustic axis. In a coordinate system constructed on vectors $\boldsymbol{p}^{(0l)}$ system (83.7) becomes

$$\rho\,(v_{01}^2-v^2)\,p_1+iQ_3p_2-iQ_2p_3=0,$$
$$-iQ_3p_1+\rho\,(v_{02}^2-v^2)\,p_2+iQ_1p_3=0, \tag{83.11}$$
$$iQ_2p_1-iQ_1p_3+\rho\,(v_{03}^2-v^2)\,p_3=0.$$

The ratio $Q/(\rho v^2)$ is always small—of the order of a/λ, where a is the lattice parameter, λ is the wavelength; we shall assume that ratios of the type $Q_3/[\rho\,(v_{02}^2 - v_{01}^2)]$ are also small, for which purpose the wave normal must be sufficiently far removed from the acoustic axes. In this case system (83.11) can be solved by approximate methods. They give

$$v_1^2 = v_{01}^2 - \frac{Q_2^2}{\rho^2\,(v_{03}^2 - v_{01}^2)} - \frac{Q_3^2}{\rho^2\,(v_{02}^2 - v_{01}^2)}, \tag{83.12}$$

$$p^{(1)} = p^{(01)} + \frac{iQ_3}{\rho\,(v_{02}^2 - v_{01}^2)}\,p^{(02)} - \frac{iQ_2}{\rho\,(v_{03}^2 - v_{01}^2)}\,p^{(03)}. \tag{83.13}$$

By means of cyclic substitution we obtain from (83.12) v_2 and v_3 and from (83.13), $p^{(2)}$ and $p^{(3)}$. A comparison of these formulas with the corresponding formulas from the theory of the optical activity of crystals (81.13) and (81.16) shows that the examined phenomenon very much reminds of the propagation of light in an optically active crystal in a direction sufficiently far removed from the optic axis (when $|\,n_{02}^{-2} - n_{01}^{-2}\,| \gg |\,G_{33}\,|$). The acoustic activity is also manifested by the polarization of waves becoming elliptic instead of linear, the ellipticity being small; the order of the ratio of the parameter characterizing the activity to the parameter characterizing the anisotropy is $G_{33}/(n_{02}^{-2} - n_{01}^{-2})$ in the theory of optical activity and $Q_3/[\rho\,(v_{02}^2 - v_{01}^2)]$ in the theory of acoustic activity. The change of velocity caused by the activity is in both cases proportional to the product of this ratio by the parameter of the activity, i.e. is of the second order of smallness.

An interesting special case of (83.13) is that of the coincidence of one of the vectors $\boldsymbol{p}^{(0l)}$ with the wave normal, which happens when the acoustic activity is not taken into consideration, and the wave is therefore longitudinal. Then the major axis of the vibration ellipse is directed along the wave normal, and the minor axis lies in the wave-front plane (cf. the vibration ellipse of vector $\boldsymbol{E}$ in case of weak optical activity, Sec. 81). This situation apparently develops on almost all longitudinal normals in crystals of class 1: on the one hand, according to F. I. Fedorov's theorem (Sec. 56), every such crystal has at least two longitudinal normals $\boldsymbol{m}^{(l)}$; on the other hand, there is no reason to expect $\boldsymbol{Q}\,(\boldsymbol{m}^{(l)})$ to be parallel to $\boldsymbol{m}^{(l)}$.

Acoustic activity, like the optical one, is most pronounced in case of the propagation of an elastic wave along one of the acoustic axes of a crystal. In this case we shall refer the Christoffel equations (83.7), for their analysis, to a system of coordinates whose two mutually orthogonal unit vectors $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ lie in the plane of the eigenvectors of tensor $\mathbf{M}$, while an isolated eigenvector $\boldsymbol{p}^{(00)}$ of tensor $\mathbf{M}$ serves as the third unit vector and $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are chosen so that the component Q_2 of vector $\boldsymbol{Q}$ would vanish:

$$\begin{aligned} \rho\,(v_{01}^2 - v^2)\,p_1 + iQ_3 p_2 &= 0, \\ -iQ_3 p_1 + \rho\,(v_{01}^2 - v^2)\,p_2 + iQ_1 p_3 &= 0, \\ -iQ_1 p_2 + \rho\,(v_{00}^2 - v^2)\,p_3 &= 0. \end{aligned} \tag{83.14}$$

To a wave with velocity $v_{(00)}$ and polarization $\boldsymbol{p}^{(00)}$, when acoustic activity is taken into consideration, there corresponds an elliptically polarized wave of small ellipticity whose velocity v_0 and the polarization vector $\boldsymbol{p}^{(0)}$ are determined by the formulas

$$v_0^2 = v_{00}^2 - \frac{Q_1^2}{\rho^2 (v_{01}^2 - v_{00}^2)}, \tag{83.15}$$

$$p^{(0)} = p^{(00)} - \frac{iQ_1}{\rho (v_{01}^2 - v_{00}^2)} e_2. \tag{83.16}$$

However, to a multitude of waves propagating with the velocity v_{01} and polarized in the directions $p^{(\varphi)}$, with acoustic activity taken into consideration, there correspond two almost circularly polarized waves; their velocities v_1 and v_2 and polarizations $p^{(1)}$ and $p^{(2)}$ are determined by the formulas

$$v_{1,2}^2 = v_{01}^2 \pm \frac{Q_3}{\rho} - \frac{Q_1^2}{2\rho (v_{00}^2 - v_{01}^2)}, \tag{83.17}$$

$$p^{(1,2)} = \frac{1}{\sqrt{2}} \left[e_1 \mp i \left(1 \mp \frac{Q_1^2}{2Q_3\rho (v_{00}^2 - v_{01}^2)} \right) e_2 \pm \frac{Q_1}{\rho (v_{00}^2 - v_{01}^2)} p^{(00)} \right]. \tag{83.18}$$

In this case too for correctly taking account of the terms of the first order of smallness in polarization vectors it is necessary to take into consideration the terms of the second order of smallness in the expressions for the velocities.

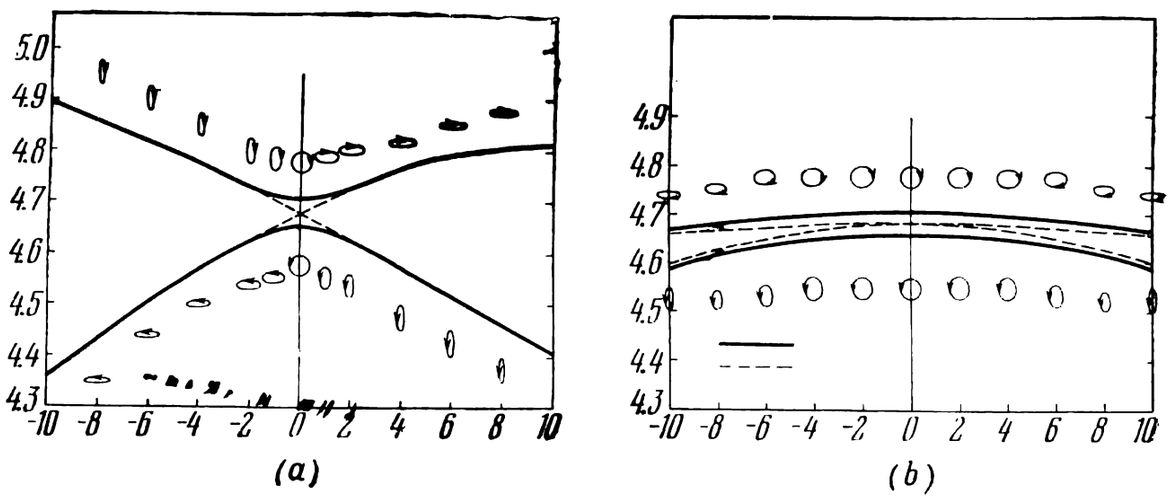


Fig. 83.1. Surfaces of normal velocities of transversal elastic waves with a frequency of 28.9 GHz and their polarization near axis X_3: (a) in α-quartz, (b) in arbitrary β-quartz. Angles from axis X_3 to axis X_2 (in degrees) are plotted on the abscissa axis, velocities in km/s are plotted on the axis of ordinates. On polarization ellipses the horizontal direction is parallel to axis X_2, the vertical direction is parallel to axis X_1. The dashed lines are the same pieces of the surfaces for low-frequency waves (Pine, 1971)

As follows from (83.17), the acoustic activity of crystals, like the optical one, results in discontinuities of the surfaces of normal velocities at the points of exit of the acoustic axes. This can be seen, for instance, in Fig. 83.1.

As was noted in Sec. 56, all the higher than two-fold symmetry axes are the longitudinal acoustic axes. If for the direction $\boldsymbol{m}$ of such an axis the pseudovector of acoustic gyration $Q(\boldsymbol{m})$ differs from zero, it is evidently parallel to the axis: $Q(\boldsymbol{m}) = Q\boldsymbol{m}$. In this case the situation is greatly simplified: the longitudinal wave does not change at all! ($v_0 = v_{00}$, $p^{(0)} = p^{(00)}$, while transversal waves

are polarized strictly circularly

$$v_{1,2}^2 = v_{01}^2 \pm \frac{Q}{\rho}, \tag{83.19}$$

$$p^{(1,2)} = \frac{1}{\sqrt{2}}(e_1 \mp e_2). \tag{83.20}$$

Thus, the rotation of the polarization plane of transversal elastic waves is observed. The specific rotation of the polarization plane in this case is

$$\alpha = \frac{Q\omega}{2\rho v_{01}^3}. \tag{83.21}$$

Since the best directions for the observation of the acoustic activity of crystals are the acoustic axes, the magnitude of the vector of acoustic gyration in the direction of these axes becomes of great importance. Let us note in this connection that in crystal of class $\bar{4}3m$ in the directions of acoustic axes $\langle 100 \rangle$ and $\langle 111 \rangle$, since these directions lie in the symmetry planes, vector Q (m) vanishes.

The polarization of transversal elastic waves propagating in crystals of α- and β-quartz (classes 32 and 622 respectively) along the principal symmetry axis and in the directions close to it, as well as the forms of the corresponding pieces of surfaces of these crystals' normal velocities are shown in Fig. 83.1*.

The acoustic activity of crystals, just as the optical one is determined by a dimensionless parameter a/λ, i.e. by the ratio of the lattice constant to the wavelength. Therefore, marked effects of acoustic activity can be obtained with supersonic elastic waves whose lengths are of the order of a micrometer and the frequencies of the order of gigahertz (Lemanov and Smolenski, 1972). The investigation of the Mandel'shtam-Brillouin scattering of light done with circularly polarized supersonic waves with the frequency of 28.9 GHz, propagating along the principal symmetry axis of a quartz crystal permitted to determine the specific rotation of the polarization plane of a supersound; at this frequency it turned out to be $1.06 \cdot 10^5$ deg/cm (Pine, 1971). Hence it is not difficult to find the components of tensors characterizing the acoustic activity of quartz: $g_{3333} = 5.58 \times 10^9$ dyn/cm^2, $b_{31233} = 1.44 \cdot 10^4$ dyn/cm. For a comparison with optical activity it is more convenient to use other quantities: the comparison of formulas (81.24) and (83.21) shows that the ratio $g_{3333}/\rho v^2 = 9.57 \cdot 10^{-3}$ is similar to the product $n_0^2 G_{33}$, the ratio $b_{31233}/\rho v^2 = 247$ pm is similar to the product $n_0^2 \gamma_{123}$, and finally, the ratio $g_{3333}\lambda/a\rho v^2 = 2.88$ is similar to the parameter $n_0^2 G_{33}\lambda/a$. Thus, when comparing these quantities with the values G_{33}, γ_{123} and $G_{33}\lambda/a$ given in Table 81.2 the latter must be multiplied by $n_0^2 \approx 2.4$. But even after performing all these operations the acoustic activity of quartz is found to be almost 100 times stronger than the optical activity.

Concerning the problems mentioned in this chapter see Agranovich and Ginsburg (1965); Akhmanov (1969); Akhmanov and Khokhlov (1964); Bier and Pikus (1972); Bloembergen (1966); de Groot, Mazur (1962); Zheludev (1968, 1969, 1976); Klimontovich (1966); Landau and Lifshits (1957); Landsberg (1957); Mason (1964); Pekara (1973); Sonin and Vasilevskaya (1971); Thurston (1967); Haase (1963).

---

* The calculation for β-quartz was done conditionally: the data for α-quartz were used, but coefficient c_{14} was assumed to equal zero.

Chapter X

SOME GENERAL PROBLEMS OF CRYSTAL PHYSICS

Sec. 84. Extreme-Value Problems of Crystal Physics

It is especially important for the practical use of crystals to determine the directions in which a given property of a crystal assumes its maximum or minimum value. Such problems arise in all branches of crystal physics, but to get an idea of the methods for their solution it will suffice to consider some single property. For this purpose we consider three problems pertaining to the theory of the piezoelectric effect.

Problem 1. How is a slab to be sawn out of a piezoelectric crystal so as to obtain a maximum density of the charge on its short-circuited plates under uniaxial stress perpendicular to the plane of the plate? The cases to be considered are the following: (a) a crystal of quartz (class 32); (b) a crystal of the class of longitudinal piezoelectric symmetry $43m$; (c) a crystal or texture of the class of longitudinal piezoelectric symmetry ∞m.

Solution. General part. As was shown in Sec. 59, the charge density under these conditions is proportional to a cubic M of the components of a unit vector of a perpendicular to the plane of the slab $\boldsymbol{n}$:

$$M(\boldsymbol{n}) = \mathbf{f} \vdots \boldsymbol{nnn} = f_{ikl} n_i n_k n_l, \tag{84.1}$$

Here $\mathbf{f}$ is the tensor of the longitudinal piezoelectric effect (see Sec. 58). It is required to find unit vectors $\boldsymbol{n}$, i.e. those satisfying the condition

$$\Phi(\boldsymbol{n}) = \boldsymbol{n}\cdot\boldsymbol{n} - 1 = 0, \tag{84.2}$$

and such that function $M(\boldsymbol{n})$ would assume its extreme value. Consider the function

$$F = M - \frac{3}{2}\lambda\Phi,$$

where λ is a so-far indefinite Lagrange's multiplier, and coefficient 3/2 is added for symplifying further calculations. We find the sought-for values of the components n_i and multiplier λ as the solutions of a system of four equations: equation (84.2) and of three equations corresponding to vector equation $\partial F/\partial \boldsymbol{n} = 0$. The latter can be written down as

$$\mathbf{f} : \boldsymbol{nn} - \lambda\boldsymbol{n} = 0, \quad f_{ikl} n_k n_l - \lambda n_i = 0. \tag{84.3}$$

By scalar multiplication of the two sides of (84.3) by $\boldsymbol{n}$, we find

$$\lambda = \mathbf{f} \vdots \boldsymbol{nnn} = f_{ikl} n_i n_k n_l. \tag{84.4}$$

Evidently, n_i here is the component of one of the vectors $\boldsymbol{n}^{(s)}$ for which function $M(\boldsymbol{n})$ attains its extreme (or at least stationary) value $\lambda_{(s)} = M(\boldsymbol{n}^{(s)})$.

Now we shall perform subsequent calculations for specific cases.

Solution of Problem 1a. Let us substitute into equation (84.3) the surviving components of the tensor of the longitudinal piezoelectric effect for the crystals of class 32 (Table 58.2). Denoting $f_{111} = -f_{122} = -f_{212} = -f_{221} = f$, we obtain

$$f(n_1^2 - n_2^2) - \lambda n_1 = 0, \tag{84.5a}$$

$$-2f n_1 n_2 - \lambda n_2 = 0, \tag{84.5b}$$

$$-\lambda n_3 = 0 \tag{84.5c}$$

while formula (84.4) will have the form

$$\lambda = fn_1 (n_1^2 - 3n_2^2).$$

We shall begin the solution of (84.5) with (84.5c). It is apparent that either $\lambda = 0$, or $n_3 = 0$. In the first case it follows from (84.5a) that $n_1^2 = n_2^2$, this being compatible with (84.5b) only if $n_1 = n_2 = 0$. Now we find from (84.2) that $n_3 = \pm 1$. Thus, the first solutions are

$$\left.\begin{aligned} \boldsymbol{n}^{(1)} &= \boldsymbol{e}_3, \\ \boldsymbol{n}^{(2)} &= -\boldsymbol{e}_3, \end{aligned}\right\} \quad \begin{aligned} &\boldsymbol{n}^{(1)},\ \boldsymbol{n}^2 \parallel \langle 0001 \rangle, \\ &\lambda_{(1)} = \lambda_{(2)} = 0. \end{aligned} \tag{84.6}$$

Let us take up the second possibility: $n_3 = 0$. From (84.5b) it follows that either $n_2 = 0$, or $2fn_1 + \lambda = 0$. In the first case $n_1 = \pm 1$ and $\lambda = \pm f$. In the second case all four combinations are possible: $n_1 = \pm 1/2$, $n_2 = \pm\sqrt{3/2}$, with $\lambda = -2n_1 f$. Thus, the following solutions are obtained:

$$\left.\begin{aligned} \boldsymbol{n}^{(3)} &= \boldsymbol{e}_1, \\ \boldsymbol{n}^{(4)} &= -\frac{1}{2}\boldsymbol{e}_1 + \frac{\sqrt{3}}{2}\boldsymbol{e}_2, \\ \boldsymbol{n}^{(5)} &= -\frac{1}{2}\boldsymbol{e}_1 - \frac{\sqrt{3}}{2}\boldsymbol{e}_2, \end{aligned}\right\} \quad \begin{aligned} &\boldsymbol{n}^{(3)},\ \boldsymbol{n}^{(4)},\ \boldsymbol{n}^{(5)} \parallel \langle 2\bar{1}\bar{1}0 \rangle, \\ &\lambda_{(3)} = \lambda_{(4)} = \lambda_{(5)} = f; \end{aligned}$$

$$\left.\begin{aligned} \boldsymbol{n}^{(6)} &= -\boldsymbol{e}_1, \\ \boldsymbol{n}^{(7)} &= \frac{1}{2}\boldsymbol{e}_1 - \frac{\sqrt{3}}{2}\boldsymbol{e}_2, \\ \boldsymbol{n}^{(8)} &= \frac{1}{2}\boldsymbol{e}_1 + \frac{\sqrt{3}}{2}\boldsymbol{e}_2, \end{aligned}\right\} \quad \begin{aligned} &\boldsymbol{n}^{(6)},\ \boldsymbol{n}^{(7)},\ \boldsymbol{n}^{(8)} \parallel \langle \bar{2}110 \rangle, \\ &\lambda_{(6)} = \lambda_{(7)} = \lambda_{(8)} = -f. \end{aligned} \tag{84.7}$$

The vectors $\boldsymbol{n}^{(3)}$, $\boldsymbol{n}^{(4)}$ and $\boldsymbol{n}^{(5)}$ are symmetrically equivalent; no wonder that one and the same value $\lambda = f$ corresponds to all of them. Three vectors to which there corresponds $\lambda = -f$ are certainly also symmetrically equivalent to one another. It is apparent that solutions (84.7) correspond to the extremums of the function $M(\boldsymbol{n})$, but to which one in particular, depends on the sign of the coefficient $f = f_{111}$. As for the solution (84.6), it does not correspond to an extremum. Thus, the two-fold axes are the extreme directions for the longitudinal piezoelectric effect in quartz crystals (and generally in crystals with the $\bar{6}m2$ symmetry of the longitudinal piezoelectric effect). All this can be seen in the stereographic projection of the representation surface of the unit septor S^0 [$\bar{6}m2$] (see Fig. 47.4); it is only necessary to note the arrangement of the coordinate axes.

Solution of Problem 1b. For crystals with the symmetry $\bar{4}3m$ of the longitudinal piezoelectric effect equations (84.3) become

$$\begin{aligned} 2fn_2n_3 - \lambda n_1 &= 0, \\ 2fn_3n_1 - \lambda n_2 &= 0, \\ 2fn_1n_2 - \lambda n_3 &= 0, \end{aligned} \tag{84.8}$$

where $f_{123} = f$. According to (84.4), $\lambda = 6fn_1n_2n_3$. Substituting λ into equation (84.8), we obtain a system

$$\begin{aligned} n_2n_3\,(1 - 3n_1^2) &= 0, \\ n_3n_1\,(1 - 3n_2^2) &= 0, \\ n_1n_2\,(1 - 3n_3^2) &= 0. \end{aligned} \tag{84.9}$$

It can be easily seen that system (84.9) has three symmetrically equivalent sets of solutions

$$\left.\begin{aligned} n^{(1,2)} &= \pm e_1, \\ n^{(3,4)} &= \pm e_2, \\ n^{(5,6)} &= \pm e_3, \end{aligned}\right\} \quad \begin{aligned} &n^{(1)}, \ldots, n^{(6)} \parallel \langle 100 \rangle, \\ &\lambda_{(1)} = \ldots = \lambda_{(6)} = 0; \end{aligned} \tag{84.10}$$

$$\left.\begin{aligned} n^{(7)} &= \frac{1}{\sqrt{3}}(e_1 + e_2 + e_3), \\ n^{(8)} &= \frac{1}{\sqrt{3}}(e_1 - e_2 - e_3), \\ n^{(9)} &= \frac{1}{\sqrt{3}}(-e_1 + e_2 - e_3), \\ n^{(10)} &= \frac{1}{\sqrt{3}}(-e_1 - e_2 + e_3), \end{aligned}\right\} \quad \begin{aligned} &n^{(7)}, \ldots, n^{(10)} \parallel \langle 111 \rangle, \\ &\lambda_{(7)} = \ldots = \lambda_{(10)} = \frac{2f}{\sqrt{3}}; \end{aligned} \tag{84.11}$$

$$\left.\begin{aligned} n^{(11)} &= \frac{1}{\sqrt{3}}(-e_1 + e_2 + e_3), \\ n^{(12)} &= \frac{1}{\sqrt{3}}(e_1 - e_2 + e_3), \\ n^{(13)} &= \frac{1}{\sqrt{3}}(e_1 + e_2 - e_3), \\ n^{(14)} &= \frac{1}{\sqrt{3}}(-e_1 - e_2 - e_3), \end{aligned}\right\} \quad \begin{aligned} &n^{(11)}, \ldots, n^{(14)} \parallel \langle \bar{1}\bar{1}\bar{1} \rangle, \\ &\lambda_{(11)} = \ldots = \lambda_{(14)} = -\frac{2f}{\sqrt{3}}. \end{aligned} \tag{84.12}$$

Evidently, in this case too the set of solutions (84.10) does not correspond to any extremum, while solutions (84.11) and (84.12) correspond to extreme values of the function $M(n)$: if coefficient $f = f_{123}$ is positive, then with any $n^{(s)}$ from (84.11) the function $M(n)$ attains its maximum value, and with $n^{(s)}$ from (84.12), its minimum value. The anisotropy of the longitudinal piezoelectric effect of such symmetry is shown by the representation surface of the septor S^0 [$43m$] whose stereographic projection is given in Fig. 47.3.

Solution of Problem 1*c*. This problem is more conveniently solved without using the method of Lagrange's undetermined multipliers. Let us denote M as a function of the angle $\vartheta = \arccos(n \cdot e_3)$ using for the purpose formulas (58.10)-(58.14) and Table 47.4:

$$M(\vartheta) = F_V \cos\vartheta + \frac{1}{8} F_S (3\cos\vartheta + 5\cos 3\vartheta). \tag{84.13}$$

Here F_V and F_S are the coefficients of the expansion of tensor $\mathbf{f}$ with respect to the unit irreducible tensors V [$\infty\, m$] and S [$\infty\, m$]. The problem reduces to the determination of the values of the angle ϑ at which function $M(\vartheta)$ will attain its extreme value. This requires the solution of the equation $dM/d\vartheta = 0$ which is reduced to the form

$$\sin\vartheta \left[-F_V + \frac{3}{16} F_S (4 - 5\sin^2\vartheta) \right] = 0. \tag{84.14}$$

Whatever are the relations between F_V and F_S, it has the solutions

$$\vartheta_{(1)} = 0, \quad \vartheta_{(2)} = \pi, \quad M(\vartheta_{(1,2)}) = \pm (F_V + F_S), \tag{84.15}$$

while for a modulo sufficiently small magnitude of the ratio F_V/F_S, exactly if inequalities

$$-\frac{3}{16} \leqslant \frac{F_V}{F_S} \leqslant \frac{3}{4}, \tag{84.16}$$

hold, it also has the solutions

$$\vartheta_{(3)} = \arcsin \sqrt{\frac{4}{5} - \frac{16}{5}(F_V/F_S)}, \qquad \vartheta_{(4)} = \pi - \vartheta_{(3)},$$

$$M(\vartheta_{(3,4)}) = \pm\left(\frac{11}{3} F_V - F_S\right)\sqrt{\frac{1}{5} + \frac{16}{5}(F_V/F_S)}. \tag{84.17}$$

Both cases—of two extremums and four extremums—can be seen in Fig. 58.1. For demarcation between the vectorial and septor types of anisotropy of the longitudinal piezoelectric effect of symmetry $\infty\, m$, it is natural to use the number of the extremums; thus in case of the fulfilment of inequalities (84.16) there takes place the septor type, and in case of its non-fulfilment, the vectorial type of anisotropy.

This example shows that although the directions connected with symmetry elements are very often extremal, the extreme values can nevertheless be attained in the directions that have nothing in common with symmetry elements.

Problem 2. How is a slab to be sawn out of a piezoelectric crystal so as to obtain an extreme density of the charge on its short-circuited plates as a result of uniaxial extension in a specified direction that lies in the plane of the slab?

Solution. As was shown in Sec. 59, the charge density under these conditions is proportional to the expression

$$M(\boldsymbol{n}) = \boldsymbol{n}\cdot\mathbf{d} : \boldsymbol{q}\boldsymbol{q} = \boldsymbol{A}\cdot\boldsymbol{n}, \tag{84.18}$$

where $\boldsymbol{n}$ is the unit vector of the perpendicular to the slab, $\mathbf{d}$ is the tensor of piezoelectric coefficients, $\boldsymbol{q}$ is the unit vector of the direction of extension, and vector $\boldsymbol{A} = \mathbf{d} : \boldsymbol{q}\boldsymbol{q}$. It is necessary to find a unit vector $\boldsymbol{n}$ perpendicular to $\boldsymbol{q}$

$$\Phi_1(\boldsymbol{n}) = \boldsymbol{n}\cdot\boldsymbol{n} - 1 = 0, \qquad \Phi_2(\boldsymbol{n}) = \boldsymbol{q}\cdot\boldsymbol{n} = 0, \tag{84.19}$$

and that would also lead to an extremum of function $M(\boldsymbol{n})$. Let us compose for this purpose a function

$$F = M - \frac{1}{2}\lambda\Phi_1 - \mu\Phi_2,$$

where λ and μ are Lagrange's undetermined multipliers. The sought-for vectors $\boldsymbol{n}$ satisfy equations (84.19) and the equation

$$\frac{\partial F}{\partial \boldsymbol{n}} = \boldsymbol{A} - \lambda\boldsymbol{n} - \mu\boldsymbol{q} = 0. \tag{84.20}$$

Having scalarly multiplied (84.20) by $\boldsymbol{q}$ and bearing in mind that $\boldsymbol{q}\cdot\boldsymbol{n} = 0$, we shall find that $\mu = \boldsymbol{A}\cdot\boldsymbol{q}$. Upon scalar multiplication of (82.20) by $\boldsymbol{n}$, we obtain $\lambda = \boldsymbol{A}\cdot\boldsymbol{n}$. Finally, upon scalar multiplication of (84.20) by $\boldsymbol{A}$, we compute $\boldsymbol{A}\cdot\boldsymbol{n} = \sqrt{A^2 - (\boldsymbol{A}\cdot\boldsymbol{q})^2}$. Substituting all quantities thus found into (84.20), we shall obtain the solution of the problem:

$$\boldsymbol{n} = \frac{(\mathbf{I} - \boldsymbol{q}\boldsymbol{q})\cdot\boldsymbol{A}}{\sqrt{A^2 - (\boldsymbol{A}\cdot\boldsymbol{q})^2}}, \qquad M = \sqrt{A^2 - (\boldsymbol{A}\cdot\boldsymbol{q})^2}. \tag{84.21}$$

Problem 3. The orientation of a slab sawn out of a piezoelectric crystal is specified by the unit vector of the perpendicular to its plane $\boldsymbol{n}$. How should

the uniaxial extension be directed in the plane of the slab, so as to obtain the extreme values of: (a) the charge density on the slab's short-circuited plates; (b) potential difference between its open-circuited plates.

Solution. The density of charges on the short-circuited plates, as well as the potential difference between the open-circuited plates, both caused by uniaxial extension, are proportional to the function

$$M(\boldsymbol{q}) = B_{kl}q_k q_l = \mathbf{B} : \boldsymbol{qq}, \tag{84.22}$$

where $\boldsymbol{q}$ is the unit vector of the direction of extension. For the charge density tensor $\mathbf{B} = \boldsymbol{n}\cdot\mathbf{d}$, and for the potential difference $\mathbf{B} = \boldsymbol{n}\cdot\mathbf{d}/(\boldsymbol{n}\cdot\boldsymbol{\varkappa}\cdot\boldsymbol{n})$; here $\mathbf{d}$ is the tensor of piezoelectric coefficients, $\boldsymbol{\varkappa}$ is the tensor of dielectric permittivity. The problem now is reduced to finding vectors $\boldsymbol{q}$ satisfying the conditions

$$\Phi_1(\boldsymbol{q}) = \boldsymbol{q}\cdot\boldsymbol{q} - 1 = 0, \qquad \Phi_2(\boldsymbol{q}) = \boldsymbol{n}\cdot\boldsymbol{q} = 0, \tag{84.23}$$

under which function $M(\boldsymbol{q})$ attains its extreme value. For this purpose an auxiliary function is composed

$$F = \frac{1}{2}M - \frac{1}{2}\lambda\Phi_1 + \mu\Phi_2$$

with Lagrange's undetermined multipliers λ and μ and a set of equations consisting of (84.23) and

$$\frac{\partial F}{\partial \boldsymbol{q}} \quad \mathbf{B}\cdot\boldsymbol{q} - \lambda\boldsymbol{q} + \mu\boldsymbol{n}, \qquad \frac{\partial F}{\partial q_k} = B_{kl}q_l - \lambda q_k + \mu n_k \tag{84.24}$$

is solved. Such a problem was investigated in detail in Sec. 37, see (37.7) and further on. It is shown there that the tensors and vectors involved in the problem can conveniently be referred to a coordinate system whose axis X_3 is directed along vector $\boldsymbol{n}$. We now find the extreme values of function $M = \mathbf{B} : \boldsymbol{qq}$, namely

$$\lambda_{(1,2)} = \frac{1}{2}\left[(B_{11} + B_{22}) \pm \sqrt{(B_{11} - B_{22})^2 + (2B_{12})^2}\right], \tag{84.25}$$

as well as a system of equations for the determination of components $q_1^{(s)}$ and $q_2^{(s)}$ $(s = 1, 2)$:

$$\begin{aligned} (B_{11} - \lambda_{(s)})\, q_1^{(s)} + B_{12}q_2^{(s)} &= 0, \\ B_{12}q_1^{(s)} + (B_{22} - \lambda_{(s)})\, q_2^{(s)} &= 0, \end{aligned} \tag{84.26}$$

while the component $q_3^{(s)} = 0$.

Generally, the extreme problems of crystal physics, as has been shown even by the few above examples, are quite amply varied and at times fairly complicated. Apparently, they are all combined not only by the common character of the problem, but also by the common method of its solution—the method of Lagrange's undetermined multipliers. Problem 1*c*, solved by another method, does not disprove but rather corroborates this conclusion: the method of undetermined multipliers could be successfully avoided only because the symmetry of the piezoelectric properties of a medium is characterized not by a crystallographic but by a limit group.

Sec. 85. The Problem of Comparing Tensor Properties of Crystals

When dealing with scalar properties of crystals, such as density and heat capacity, it is not difficult to determine when the properties of two substances coincide or are close in their magnitudes. In this

case there is no problem at all. If we pass to the investigation of vector properties, say, of pyroelectric coefficients, then the problem of comparing these properties arises, although in this case it is also easily solved: the pyroelectric properties of two crystals are obviously the same, if the sums of the squares of pyroelectric coefficients coincide:

$$p_i^{(1)} p_i^{(1)} = p_j^{(2)} p_j^{(2)}. \tag{85.1}$$

These properties are close to each other, if the left- and right-hand sides of expression (85.1), though not being equal, differ but little. Thus, tourmaline, a crystal of class $3m$, with its vector of pyroelectric coefficients $\boldsymbol{p}^{(1)} = 1.2\boldsymbol{e}_3$ (in aesu) would be very closely approached, in respect of pyroelectric properties, by a hypothetical crystal of class 1 with the vector of pyroelectric coefficients $\boldsymbol{p}^{(2)} = 0.4\boldsymbol{e}_1 + 0.8\boldsymbol{e}_2 + 0.8\boldsymbol{e}_3$ (in the same units).

The problem of comparison of properties still remains fairly simple if the property that interests us is described by a symmetric second-rank tensor: for such properties to coincide it is necessary and sufficient that the eigenvalues of the compared matter tensors coincide.

Let us examine the problem of the comparison of an arbitrary tensor property in two crystals belonging to one class. To be more precise, we shall assume that the form of the corresponding matter tensor is the same in both crystals.

Two cases are to be distinguished here. If in a given tensor the number of independent invariants and of independent components is the same, the necessary and sufficient condition for the properties to coincide is the equality of all the components of the matter tensor of one crystal to the corresponding components of the matter tensor of the other crystal: $A_i^{(1)} \ldots {}_k = A_i^{(2)} \ldots {}_k$.

If, however, the numbers of independent components and independent invariants of the given matter tensor do not coincide, the problem becomes much more complicated. As was explained in Sec. 47, a tensor, as a geometric object, is characterized by its invariants. If there are more independent components than independent invariants, it means that the crystal's symmetry admits of rotation of a matter tensor of the given type, as of a solid, with respect to the crystal structure (and the crystal-physical system of coordinates connected with it). It can happen in this case that the non-coincidence of the components of the two matter tensors with respect to the crystal-physical frames of reference is caused not by the difference between these tensors as geometric objects, but simply by their being differently oriented with respect to the frames. It follows that prior to comparing such tensors they should be similarly oriented; if matter tensors are oriented in the same way, then in case of the coincidence of a corresponding property all the components of one

tensor will also be equal to the corresponding components of the other tensor.

The problem of comparison of the tensor properties has now become one of attaining similar orientation of two matter tensors. Let us consider two examples.

A comparison is made of the piezoelectric properties of two crystals of class m. The tensor of piezoelectric coefficients **d** for this class has 10 independent components, but only 9 invariants; the "excess" component characterizes the rotation of the tensor in the symmetry plane $m \perp X_2$. Let us examine vector $\mathbf{d} = \mathbf{d} : \mathbf{I}$ with components $d_i = d_{ikk}$ which characterizes the piezoelectric effect under the influence of hydrostatic compression. In class m this vector is (see Table 58.2)

$$\mathbf{d} = (d_{11} + d_{12} + d_{13})\, \boldsymbol{e}_1 + (d_{31} + d_{32} + d_{33})\, \boldsymbol{e}_3 = d_1\boldsymbol{e}_1 + d_3\boldsymbol{e}_3. \tag{85.2}$$

Let us call the system of coordinates, X_1', X_2', X_3' of tensor **d** proper if its axis X_1' is directed along vector **d**; the angle φ of its rotation with respect to the crystal-physical coordinate frame X_1, X_2, X_3 is determined from the equation

$$d_{3'} = d_1 \sin\varphi + d_3 \cos\varphi = 0 \tag{85.3}$$

with an additional condition

$$d_{1'} = d_1 \cos\varphi - d_3 \sin\varphi > 0. \tag{85.4}$$

Having referred each tensor to its proper system we can compare the tensors' components.

We want to emphasize that proper coordinate frame can be introduced by other methods too (e.g., it is possible to call frame X_1'', X_2'', X_3'' proper if it is determined by conditions $d''_{322} = 0$, $d''_{122} > 0$); any reasonably defined proper system is suitable for the comparison of matter tensors.

Following Novozhilov (1958, Ch. V, Secs. 19, 20), we shall also discuss the comparison of elastic properties of crystals of the triclinic system. The tensor of the elastic compliance coefficients s has 21 independent components and only 18 independent invariants. For its proper coordinate system we can use, let us say, a system constructed on the eigenvectors of a symmetric second-rank tensor $\mathbf{S} = \mathbf{s} : \mathbf{I}$ (its components being $S_{ij} = s_{ijkk}$). To compare the components of the elastic compliance tensors of different crystals it is first necessary to refer each tensor to its proper coordinate frame. In this case a proper system can also be chosen differently, e.g. by constructing it on the eigenvectors of a symmetric second-rank tensor **Z** with components $Z_{ij} = s_{ikjk}$ (see Tables 53.1 and 54.1).

Let us now pass to the problem of comparison of the tensor properties of crystals of different classes when the compared tensors have different forms; we shall restrict ourselves to the case most important for crystal physics—when one of the classes is a subgroup of the other.

We shall immediately give some examples. It is necessary, for instance, to compare the elastic properties of cubic and tetragonal modifications of barium titanate crystals. These modifications differ only by a small displacement of atoms (see Sec. 64) and it is naturally required, for the comparison of their elastic properties, that the coordinate frames in both modifications would be similarly oriented with respect to structure. In this case the elementary cell of the tetragonal modification differs from the cell of the cubic modification only by a small strain in the direction of the tetragonal axis. Therefore, the standard crystal-physical systems of coordinates are already similarly oriented with respect to structure, so that we can directly compare the tabulated values of the components of the elastic compliance tensors of both modifications of barium titanate.

A crystal of tungsten trioxide, WO_3, also has a cubic and a tetragonal modification, and one of them is obtained from the other merely by a small displacement of atoms, but the elementary cell of the tetragonal modification essentially differs from that of the cubic modification: one of its edges coincides with that of the cubic cell, while the other two edges coincide with the diagonals of the cubic cell faces. Therefore crystal-physical frames of both modifications are differently oriented with respect to structure; to obtain similar orientation of the two frames with respect to structure one of the crystal-physical coordinate systems, say the tetragonal one, must be rotated by 45° about the tetragonal axis. Although in the rotated system the elastic compliance coefficients tensor will have the same general form as in the initial crystal-physical frame, its components will be changed; as can be easily calculated, the components of the "rotated" tensor will be expressed in terms of the components of the initial one as follows:

$$\begin{bmatrix} s_{11}-a/2 & s_{12}+a/2 & s_{13} & 0 & 0 & 0 \\ & s_{11}-a/2 & s_{13} & 0 & 0 & 0 \\ & & s_{33} & 0 & 0 & 0 \\ & & & s_{44} & 0 & 0 \\ & & & & s_{44} & 0 \\ & & & & & s_{66}+2a \end{bmatrix}, \qquad (85.5)$$

where $a = s_{11} - s_{12} - s_{66}/2$. Exactly the linear combinations given in this Table, and not the crystal-physical elastic compliance coef-

ficients of the tetragonal modification of tungsten trioxide at all, are to be compared with the corresponding components of the elastic compliance tensor of the cubic modification.

A similar situation arises in case of the comparison of the piezoelectric and elastic properties of two crystal modifications of zinc sulphide, ZnS—sphalerite (class $\bar{4}3m$) and würtzite (class $6mm$). For a direct comparison of piezoelectric and elastic compliance coefficients of both modifications we shall write down the matter tensors of the cubic modification in a frame in which axis X_3 is directed along the three-fold axis, and X_1 along the perpendicular to one of the symmetry planes passing through it*. The tensor of the elastic compliance coefficients will in this case have the following form

$$\begin{bmatrix} s_{11}-a/2 & s_{12}+a/6 & s_{13}+a/3 & a\sqrt{2}/3 & 0 & 0 \\ & s_{11}-a/2 & s_{13}+a/3 & -a\sqrt{2}/3 & 0 & 0 \\ & & s_{11}-2a/3 & 0 & 0 & 0 \\ & & & s_{44}+4a/3 & 0 & 0 \\ & & & & s_{44}+4a/3 & 2a\sqrt{2}/3 \\ & & & & & s_{44}+2a/3 \end{bmatrix}, \tag{85.6}$$

where $a = s_{11} - s_{12} - s_{44}/2$, and the tensor of piezoelectric coefficients has the form

$$\begin{bmatrix} 0 & 0 & 0 & 0 & -d/\sqrt{3} & 2d/\sqrt{6} \\ d/\sqrt{6} & -d/\sqrt{6} & 0 & -d/\sqrt{3} & 0 & 0 \\ -d/2\sqrt{3} & -d/2\sqrt{3} & d/\sqrt{3} & 0 & 0 & 0 \end{bmatrix}, \tag{85.7}$$

where $d = d_{14}$. Only upon writing the tensor of elastic compliance coefficients of sphalerite in the form (85.6) and the tensor of its piezoelectric coefficients in the form (85.7) it will be worthwhile to compare these tensors with the corresponding matter tensors of würtzite.

The last example: let us compare the dielectric, piezoelectric and elastic properties of two crystal modifications of potassium dihydrophosphate—the tetragonal (class $\bar{4}2m$) and the rhombic (class $mm2$)

* Thus we compare class $\bar{4}3m$ not with class $6mm$ to which würtzite belongs, but with class $3m$ since the latter, in distinction from $6mm$, is actually a subgroup of group $43m$. Then, generally speaking, the tensors of the hexagonal modification should be referred to the crystal-physical system of class $3m$, but this is not necessary, since the given tensors satisfy the conditions of Hermann's theorem.

ones. From the rules for the choice of crystal-physical systems of coordinates (see Appendix A) it is apparent that prior to comparing the tensor properties of these two modifications it is necessary to refer the tensors of one of them to a system of coordinates rotated with respect to the crystal-physical system through 45° about axis X_3. The phase transition connecting these two modifications was discussed in Sec. 65 (see also Tables 64.1 and 65.1); for our discussion it would be more convenient to refer the matter tensors of the tetragonal modification to the crystal-physical coordinate system, and the matter tensors of the rhombic modification, to the rotated one. In this case the latter tensors will have the following form

$$[\varkappa_{i'j'}] = \begin{bmatrix} \frac{\varkappa_{11}+\varkappa_{22}}{2} & \frac{\mp\varkappa_{11}\mp\varkappa_{22}}{2} & 0 \\ & \frac{\varkappa_{11}+\varkappa_{22}}{2} & 0 \\ & & \varkappa_{33} \end{bmatrix}, \tag{85.8}$$

$$[d_{i'\lambda'}] = \begin{bmatrix} 0 & 0 & 0 & \frac{\mp d_{24}\mp d_{15}}{2} & \frac{d_{24}+d_{15}}{2} & 0 \\ 0 & 0 & 0 & \frac{d_{24}+d_{15}}{2} & \frac{\pm d_{24}\mp d_{15}}{2} & 0 \\ \frac{d_{31}+d_{32}}{2} & \frac{d_{31}+d_{32}}{2} & d_{33} & 0 & 0 & \pm d_{32}\mp d_{31} \end{bmatrix}, \tag{85.9}$$

$$[s_{\lambda'\mu'}] = \begin{bmatrix} \frac{s_{11}+s_{12}-a}{2} & \frac{2s_{12}+a}{2} & \frac{s_{13}+s_{23}}{2} & 0 & 0 & \frac{\mp s_{11}\pm s_{22}}{2} \\ & \frac{s_{11}+s_{12}-a}{2} & \frac{s_{13}+s_{23}}{2} & 0 & 0 & \frac{\mp s_{11}\pm s_{22}}{2} \\ & & s_{33} & 0 & 0 & \frac{\mp s_{13}\pm s_{23}}{2} \\ & & & \frac{s_{44}+s_{55}}{2} & \frac{\pm s_{44}\mp s_{55}}{2} & 0 \\ & & & & s_{44}+s_{55} & 0 \\ & & & & & s_{66}+2a \end{bmatrix}, \tag{85.10}$$

where $a = 1/2\,(s_{11} + s_{22} - 2s_{12} - s_{66})$.

The given combinations of the tabulated (crystal-physical) components of the matter tensors of the rhombic modification of potassium dihydrophosphate can be compared with their tabulated values for the tetragonal modification of this substance. Just this was done in Table 65.1. Some components have indefinite signs because symmetry planes equivalent in class $\bar{4}2m$ become unequivalent in class

$mm2$, and we do not know yet to which of the symmetry planes the crystal-physical axis X_1 of the rhombic modification is perpendicular and to which axis X_2 is perpendicular; to find this out it is necessary to measure or at least to compare the parameters of the elementary cell of the rhombic modification.

In this Section the problem of comparison of the tensor properties of crystals was investigated in the examples of dielectric, piezoelectric and elastic properties. The same methods can be used to compare other tensor properties of crystals.

Sec. 86. The Problem of Choosing Standard Crystallographic and Crystal-Physical Systems of Coordinates

Let us imagine a situation, quite usual nowadays: at two different laboratories there has been independently synthesized one and the same crystal and its properties are being investigated. For the workers of the two laboratories to describe their crystals similarly, they have to make the same choice of crystallographic and crystal-physical coordinate systems, for which purpose there are needed some commonly used and distinctly unambiguous rules.

We describe here the existing recommendations for the choice of coordinate systems and discuss the possibilities for improving them. The point is that there are commonly accepted rules to choose the crystallographic coordinate axes, X, Y, Z, in each system (see Sec. 4). There are also widely used rules for connecting the crystallographic axes, X, Y, Z, with the crystal-physical axes X_1, X_2, X_3. These rules state the following: when the crystallographic coordinate system is rectangular, axes X_1, X_2, X_3 coincide with axes X, Y, Z respectively; in crystals of the hexagonal system axes X_3 and X_1 coincide with axes Z and X respectively; in crystals of the monoclinic system axes X_2 and X_3 coincide with axes Y and Z respectively; finally, in crystals of the triclinic system axis X_3 coincides with axis Z, while axis X_1 lies in plane (010), i.e. XZ. These rules are given in Table A.2, and Tables A.1 and B.1 were composed in conformance with them. The formulation of the rules is given in the IRE Standards on Piezoelectric Crystals (1949); see also Mason (1952). But it is necessary still to choose the positive directions on the axes, and to decide which of the symmetrically equivalent axes should be denoted, say, by X and which by Y. Structural data are insufficient for the purpose; use has to be made of the results of some crystal-physical measurements. Corresponding recommendations are contained in the IRE Standards (1949), but unfortunately, they refer only to piezoelectric crystals. Besides, before applying these recommendations to some enantiomorphous crystal, it must be known whether the given crystal is right- or left-handed, while the recommendations do not say which crystals should be called right-handed and which ones, left-handed (except for quartz crystals to which a special section is devoted).

Below we give the rules for the choice of coordinate frames suitable for all crystallographic classes; they comply as far as possible with the recommendations of IRE. Moreover, we suggest some general rules for the choice of the right-handed modification from two enantiomorphous ones. Let us first consider these rules using tetragonal crystals as an example.

If, according to the general rules (see Sec. 4), in any crystal of the tetragonal system a coordinate system A (Fig. 86.1) is introduced, then systems B, C, ..., H connected with A by symmetry operations of class 422 also conform to the rules for the choice of crystallographic coordinate axes; these rules do not make it possible to distinguish one of these frames from another. In classes

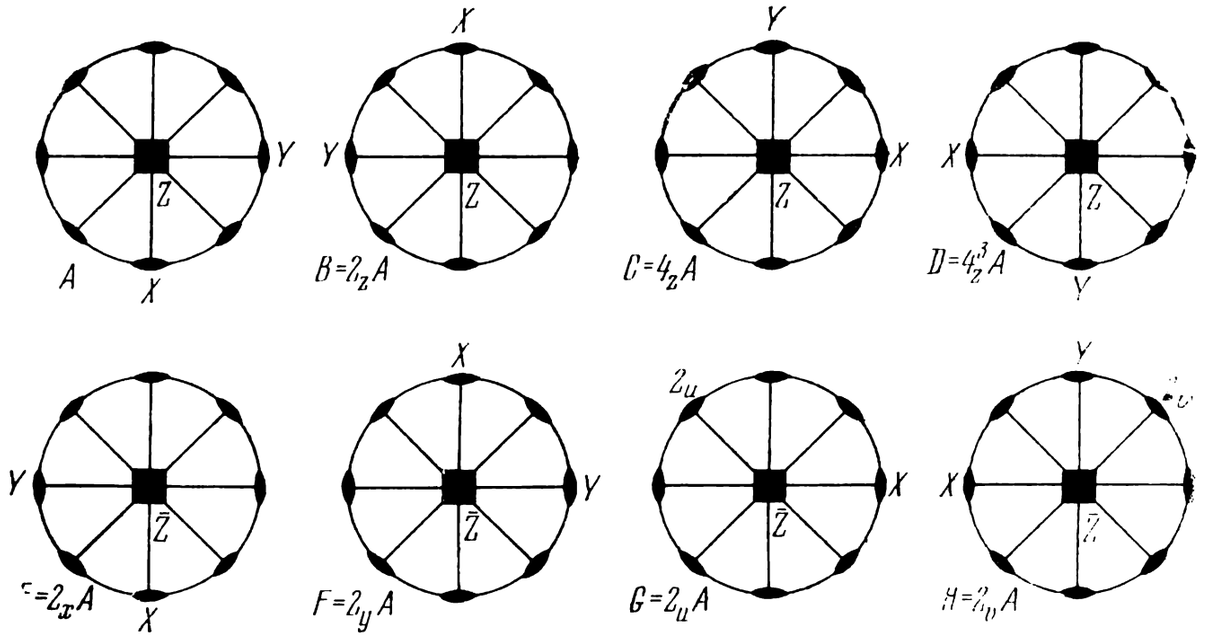


Fig. 86.1. To the choice of the denominations and positive directions alon the coordinate axes in crystals of the tetragonal system

$4/mmm$ and 422 all these systems are symmetrically equivalent, so that the distinctions between them are impossible and unnecessary. But in other classes these eight systems are segregated into sets of symmetrically equivalent systems, as shown in the following Table:

Classes	Transformations of the first kind	Sets of equivalent systems
$4mm$, $4/m$, $\overset{3}{z}$	1, 2_z, 4_z 4_z^3	$\{A, B, C, D\}$; $\{E, F, G, H\}$
$\bar{4}2m$	1, 2_z, 2_x, 2_y	$\{A, B, E, F\}$; $\{C, D, G, H\}$
$\bar{4}$	1, 2_z	$\{A, B\}$; $\{C, D\}$; $\{E, F\}$; $\{G, H\}$

The notation for the transformations and coordinate systems are the same here as in Fig. 86.1; the coordinate systems belonging to one set are enclosed in braces. Systems belonging to different sets are not symmetrically equivalent; they can (and must) differ from one another.

In classes $4mm$ and $\bar{4}2m$ we shall use IRE recommendations to choose one of the sets of coordinate systems possible in crystals of these classes: in class $4mm$ we shall choose the set with respect to which the piezoelectric coefficient d_{33} is positive, in class $\bar{4}2m$ the set with respect to which coefficient d_{36} is positive.

Class $4/m$ is centrosymmetric, has no piezoelectric properties and is therefore not mentioned in the IRE Standards (1949). However, the coordinate systems permissible in this class are segregated into two sets (see Table); let us agree to choose the one with respect to which the elastic compliance coefficient s_{16} is positive (it can be easily verified that symmetry operations transforming one set into the other reverse the sign of this coefficient, thus $2_x s_{16} = -s_{16}$).

The same rule can be used for choosing one of the two sets possible in class 4 and one pair of sets of the two pairs possible in class $\bar{4}$. To choose one set of the remaining pair we will additionally demand a positive value of coefficient

d_{36}. Let us note that group 4 is the only common subgroup for groups $4/m$ and $\bar{4}2m$, so that it is natural to combine for class $\bar{4}$ the rules used in classes $4/m$ and $\bar{4}2m$; exactly this has been done here.

It remains to point out the rules permitting to call one of the enantiomorphous modifications of classes 422 and 4 the right-handed one. Let us agree to call right-handed that of the modifications of class 422 for which the piezoelectric coefficient d_{14} is positive, and that of the modifications of class 4 for which the piezoelectric coefficient d_{33} is positive. The coefficients are considered with respect to the introduced right-handed symmetrically equivalent coordinate systems for a given class; the essential point being the choice of the set in class 4 in accordance with the centrosymmetric property (elasticity), which is manifested exactly in the same way in both enantiomorphous modifications. Generally, any piezoelectric coefficients could be used for the determination of the right-handed modification, and, moreover, any non-zero components of an odd-type matter tensor (see Sec. 44) in the corresponding classes would do the job.

The methods for an unambiguous choice of crystallographic and crystal-physical coordinate frames could be investigated in accordance with the above example for each crystal system separately, but it is more expedient to formulate general rules for all crystallographic classes on the basis of this example.

Let us agree to choose right-handed crystallographic and crystal-physical systems of coordinates and acute angles between positive directions of the corresponding crystallographic and crystal-physical axes (X and X_1, Y and X_2, Z and X_3). Therefore, the choice of the positive direction on a crystallographic axis (say, X) determines the positive direction on a corresponding crystal-physical axis (X_1), and vice versa. It is also conventional to have an obtuse angle β between positive directions of the axes X and Z in crystals of the monoclinic system, and besides the obtuse angle β, the angle α between positive directions of the axes Y and Z in crystals of the triclinic system should also be obtuse. These restrictions, together with the choice of a right-handed coordinate system, determine the positive directions on the crystallographic axes of the triclinic and monoclinic systems.

The rules for the choice of crystallographic axes and positive directions on them determine not just one but $n/2$ coordinate systems rotated with respect to each other (n is the order of the symmetry group of the holohedral class of a given crystal system), interconnected by transformations of the first kind contained in the symmetry group of the holohedral class, or, which is the same, by all symmetry transformations of an enantiomorphous hemihedral class (see Table 86.1). All these systems are symmetrically equivalent in crystals of the holohedral and enantiomorphous hemihedral classes; therefore there arises no question of the choice of positive directions on the axes or of the denominations of axes for crystals of these classes. With respect to symmetry operations in other classes these $n/2$ coordinate systems will constitute two or four sets of symmetrically equivalent systems ($n/4$ or $n/8$ systems in each set). The number of such sets for each class is given in Table 86.1. The systems of one set are connected with those of the other sets by symmetry transformations of an enantiomorphous hemihedral class of the same crystal system not contained in the set of the given class.

The choice of positive directions on the coordinate axes or of the denominations of axes is reduced to the choice of one of the two or four possible sets. In this case one has to be guided by the crystal-physical criteria (since the crystallographic ones have already been exhausted) and to use sets consisting of crystal-physical systems obtained from the crystallographic ones according to the accepted rules. The crystal-physical coordinate systems contained in one set are symmetrically equivalent, and those contained in different sets are not equivalent. Therefore any matter tensor of a crystal in all systems contained in one set has the same components, while in systems belonging to different sets some matter tensors can (although not necessarily) have different components.

Table 86.1

Methods of the Choice of Coordinate Systems and Right-Hand Modifications in 32 Crystallographic Classes

Systems	Crystallographic classes							
	holohedral	hemihedral			tetartohedral			ogdohedral
		enantiomorphous	hemimorphous	paramorphous	enantiomorphous	hemimorphous	paramorphous	enantiomorphous
Triclinic	$\{\bar{1}$	$1\}$						
Monoclinic	$\{2/m$	2	$m\}$					
Rhombic	$\{mmm$	222	$mm2\}$					
Tetragonal	$\{4/mmm$	422	$4mm$, $\bar{4}2m\}$	$\{4/m$	4	$\bar{4}\}$		
Hexagonal — hexagonal	$\{6/mmm$	622	$6mm$, $\bar{6}m2\}$	$\{6/m$	6	$\bar{6}\}$		
Hexagonal — trigonal				$\{\bar{3}m$	32	$3m\}$	$\{\bar{3}$	$3\}$
Cubic	$\{m3m$	432	$\bar{4}3m\}$	$\{m3$	$23\}$			
Number of sets	1	1	2	2	2	4	4	4
Choice of coordinate system	—	—	1 odd	1 even	1 even	1 even 1 odd	2 even	2 even
Choice of right-hand modification	—	1 odd	—	—	1 odd	—	—	1 odd

Notes. Braces combine classes included in one subsystem; on the left is the higher subsystem of the given system, on the right is the lower subsystem. "The number of sets" shows how many different sets of symmetrically equivalent coordinate systems, satisfying all crystallographic requirements, have the crystals of the given classes. "Choice of coordinate system" and "Choice of right-hand modification" show the number of the components of matter tensors, of even or odd type, for which it is necessary to determine the signs — so as to choose the coordinate system and the right-hand modification.

In principle a matter tensor can always be found in which at least one component reverses its sign under transition from one set to another; in the class in which these sets combine into one, the given component vanishes. The choice of one of the two sets will be determined, if it is convened to use for each crystal the set with respect to which the given component is positive.

The crystals of paramorphous, i.e. non-holohedral centrosymmetric classes, have only centrosymmetric properties, therefore for the choice of the set there have to be used even-type tensors which have more independent components in the given paramorphous class than in the corresponding holohedral class (if the given class is tetartohedral, then more than in the paramorphous hemihedral class). In trigonal and tetragonal systems this condition is already satisfied by the elastic tensors, but for hexagonal and cubic systems piezooptical tensors have to be used.

The choice of the coordinate system adopted for the paramorphous class is naturally extended to the whole subsystem (see Sec. 44) to which it belongs. In this case it is found that the choice is determined exclusively by even-type tensors not only in paramorphous but also in enantiomorphous (tetartohedral and ogdohedral) classes*.

The choice of a set in hemimorphous classes requires a component of an odd-type matter tensor; let us agree to use for this purpose the first non-zero piezoelectric coefficient from the following sequence

$$d_{33},\ d_{11},\ d_{22},\ d_{36},\ d_{14} \tag{86.1}$$

(the sequence is used in the IRE Standards (1949) with coefficient d_{31} instead of d_{14}). Here, for the choice of the set in a tetartohedral hemimorphous class such a coefficient should be used which vanishes in a tetartohedral enantiomorphous class of the same system.

According to the above rules, a coordinate system is chosen in the same way both in right- and left-handed crystals of any enantiomorphous class, since only centrosymmetric tensors are used for making the choice. As to non-centrosymmetric tensors, they can be used thereupon for the determination of the right-handed modification, since with respect to the introduced system of coordinates their components in the right- and left-handed modifications of the same substance are equal in absolute value and opposite in sign. Let us agree to call right-handed those crystals in which the first non-zero piezoelectric coefficient of sequence (86.1) is positive. In class 432 in which all the piezoelectric coefficients are zero, we shall call right-handed the modification in which the coefficient of gyration (see Sec. 81) is positive.

Table 86.1 shows what classes are called holohedral, hemihedral and so forth, how they are distributed among the subsystems, how many sets they have, and components of what tensors—of even or odd type—are necessary for the choice of a coordinate system and for the determination of a right-handed modification. The rules themselves for the choice of standard crystallographic and crystal-physical coordinate systems for all the 32 classes and the rules for the choice of the right-handed modification in the 11 enantiomorphous classes are combined into Table A.2.

At the end of Table A.2 there is a subdivision "Possible Changes", where it is shown how the rules for the choice of coordinate axes and enantiomorphous modifications will change if another orientation is adopted for crystals of all classes of the monoclinic system $Z \parallel 2$ or $Z \perp m$ and class $\bar{6}m2$, which in this orientation ($Z \parallel \bar{6}$, $X \parallel 2$) would be natural to denote $\bar{6}2m$. Just in this way were chosen the crystal-physical systems of coordinates in the classical manuals

* The use of centrosymmetric tensors essentially distinguishes these recommendations from the IRE Standards (1949), where only odd-type tensors are used, namely piezoelectric ones.

(Voigt, 1928; Shubnikov, Flint and Bokyi, 1940), and in some respects this choice is to be preferred.

Here we discuss the general methods and not the concrete ways of choosing standard coordinate systems. It may occur that for practical use not the suggested piezoelectric coefficients but some others can be more convenient; moreover, electrostriction tensors can be used instead of piezooptical ones, and electrooptical tensors instead of piezoelectric ones. The essence of the method will not be altered thereby.

Sec. 87. Functional Relations in Crystal Physics

So far we have assumed that nonlinear terms are small increments to the principal linear terms. With the increase in the intensity of the applied influences and in the precision of measurements, material equations of crystal physics become overgrown with an increasing number of quadratic, cubic and other increments. But instead of considering, let us say, the expansion

$$D_i = \varkappa_{ij}^{(1)} E_j + \varkappa_{ijk}^{(2)} E_j E_k + \varkappa_{ijkl}^{(3)} E_j E_k E_l + \varkappa_{ijklm}^{(4)} E_j E_k E_l E_m + \dots \quad (87.1)$$

and analyzing what is the exact form of tensors $\varkappa^{(1)}$, $\varkappa^{(2)}$, $\varkappa^{(3)}$, $\varkappa^{(4)}$, . . . for the given class of crystal symmetry, a more general problem can be formulated at the very beginning: what restrictions should be superimposed on the functional dependence of vector $\boldsymbol{D}$ upon vector $\boldsymbol{E}$ so that this dependence is compatible with the crystal's symmetry?

Quite similarly, instead of analyzing generalizations of Hooke's law

$$\varepsilon_\lambda = s_{\lambda\mu}^{(1)} \sigma_\mu + s_{\lambda\mu\nu}^{(2)} \sigma_\mu \sigma_\nu + s_{\lambda\mu\nu\rho}^{(3)} \sigma_\mu \sigma_\nu \sigma_\rho + \dots \quad (87.2)$$

the question can be raised of the general form of functional dependence of one symmetric second-rank tensor on another compatible with the crystal's symmetry.

The linear dependence of one vector on another is determined by a general second-rank tensor with internal symmetry V^2, while the linear dependence of one symmetric second-rank tensor on another is determined by a tensor with internal symmetry $[V^2]^2$. The most general form of a functional dependence of one vector on another, or of one tensor on another, compatible with the crystal's symmetry is a generalization of just such a connection determined in a linear case by matter tensors of the types V^2 and $[V^2]^2$ respectively. However, the connections most essential for crystal physics between two vectors and between two tensors, are determined by symmetric matter tensors of types $[V^2]$ and $[[V^2]^2]$. Indeed, at least in the isothermal and adiabatic processes, the linear connection between the vectors of tension and electric field induction is determined by a matter tensor of type $[V^2]$, while between the strain and stress tensors, by a matter tensor of type $[[V^2]]$. The proofs of these tensors' symmetry are based on the existence of certain potentials,

Table 87.1

Vector Potentials $\Phi(A)$ and General Vector Functions $V(A)$ Compatible with the Symmetry of Crystals and Textures

Series 1, $f=f(A_x,\ A_y,\ A_z)$:

Class 1: $\Phi=f,\ V=f_1\boldsymbol{i}+f_2\boldsymbol{j}+f_3\boldsymbol{k}$.

Series m, $f=f(A_x,\ A_y,\ A_z^2)$:

Class m ($m\perp Z$): $\Phi=f,\ V=f_1\boldsymbol{i}+f_2\boldsymbol{j}+A_zf_3\boldsymbol{k}$.

Series $mm2$, $f=f(A_z,\ A_x^2,\ A_y^2)$:

Class $mm2$: $\Phi=f,\ V=f_1\boldsymbol{k}+A_xf_2\boldsymbol{i}+A_yf_3\boldsymbol{j}$;

Class 2 ($2\parallel Z$): $\Phi=f_0+A_xA_yf_1,\ V=V(mm2)+A_yf_4\boldsymbol{i}+A_xf_5\boldsymbol{j}+A_xA_yf_6\boldsymbol{k}$.

Series mmm, $f=f(A_x^2,\ A_y^2,\ A_z^2)$:

Class mmm: $\Phi=f,\ V=A_xf_1\boldsymbol{i}+A_yf_2\boldsymbol{j}+A_zf_3\boldsymbol{k}$;

Class 222: $\Phi=f_0+A_xA_yA_zf_1\quad V=V(mmm)+A_yA_zf_4\boldsymbol{i}+A_zA_xf_5\boldsymbol{j}+$
$+A_xA_yf_6\boldsymbol{k}$;

Class $2/m$ ($2\parallel Z$): $\Phi=f_0+A_xA_yf_1,\ V=V(mmm)+A_yf_4\boldsymbol{i}+$
$+A_xf_5\boldsymbol{j}+A_xA_yA_zf_6\boldsymbol{k}$;

Class $\bar{1}$: $\Phi=f_0+A_yA_zf_1+A_zA_xf_2+A_xA_yf_3,\ V=V(2/m)+$
$+A_xf_7\boldsymbol{k}+A_yf_8\boldsymbol{k}+A_zf_9\boldsymbol{i}+A_zf_{10}\boldsymbol{j}+A_xA_yA_zf_{11}\boldsymbol{i}+A_xA_yA_zf_{12}\boldsymbol{j}$.

Series $4mm$, $f=f(A_z,\ A_x^2+A_y^2,\ A_x^2A_y^2)$:

Class $4mm$: $\Phi=f,\ V=f_1\boldsymbol{k}+f_2(A_x\boldsymbol{i}+A_y\boldsymbol{j})+A_xA_yf_3(A_y\boldsymbol{i}+A_x\boldsymbol{j})$;

Class 4: $\Phi=f_0+A_xA_y(A_x^2-A_y^2)f_1,\ V=V(4mm)+$
$+f_4(A_y\boldsymbol{i}-A_x\boldsymbol{j})+A_xA_yf_5(A_x\boldsymbol{i}-A_y\boldsymbol{j})+A_xA_y(A_x^2-A_y^2)f_6\boldsymbol{k}$.

Series $4/mmm$, $f=f(A_z^2,\ A_x^2+A_y^2,\ A_x^2A_y^2)$:

Class $4/mmm$: $\Phi=f,\ V=A_zf_1\boldsymbol{k}+f_2(A_x\boldsymbol{i}+A_y\boldsymbol{j})+A_xA_yf_3(A_y\boldsymbol{i}+A_x\boldsymbol{j})$;

Class 422: $\Phi=f_0+A_xA_yA_z(A_x^2-A_y^2)f_1,\ V=V(4/mmm)+$
$+A_zf_4(A_y\boldsymbol{i}-A_x\boldsymbol{j})+A_xA_y(A_x^2-A_y^2)f_5\boldsymbol{k}+A_xA_yA_zf_6(A_x\boldsymbol{i}-A_y\boldsymbol{j})$;

Class $\bar{4}2m$: $\Phi=f_0+A_xA_yA_zf_1,\ V=V(4/mmm)+A_xA_yf_4\boldsymbol{k}+$
$+A_zf_5(A_y\boldsymbol{i}+A_x\boldsymbol{j})+A_xA_yA_zf_6(A_x\boldsymbol{i}+A_y\boldsymbol{j})$;

Class $4/m$: $\Phi=f_0+A_xA_y(A_x^2-A_y^2)f_1,\ V=V(4/mmm)+$
$+f_4(A_y\boldsymbol{i}-A_x\boldsymbol{j})+A_xA_yf_5(A_x\boldsymbol{i}-A_y\boldsymbol{j})+A_xA_yA_z(A_x^2-A_y^2)f_6\boldsymbol{k}$;

Class 4: $\Phi=\Phi(4/m)+A_xA_yA_zf_2+A_z(A_x^2-A_y^2)f_3,\ V=V(4/m)+$
$+(A_x^2-A_y^2)f_7\boldsymbol{k}+A_xA_yf_8\boldsymbol{k}+A_zf_9(A_x\boldsymbol{i}-A_y\boldsymbol{j})+A_zf_{10}(A_y\boldsymbol{i}+A_x\boldsymbol{j})+$
$+A_xA_yA_zf_{11}(A_x\boldsymbol{i}+A_y\boldsymbol{j})+A_xA_yA_zf_{12}(A_y\boldsymbol{i}-A_x\boldsymbol{j})$.

Series $3m$, $f=f(A_z,\ A_x^2+A_y^2,\ A_y^3-3A_x^2A_y)$:

Class $3m$ ($m\perp X$): $\Phi=f$, $V=f_1\boldsymbol{k}+f_2(A_x\boldsymbol{i}+A_y\boldsymbol{j})+$
$+f_3(2A_xA_y\boldsymbol{i}+A_x^2\boldsymbol{j}-A_y^2\boldsymbol{j})$;

Class 3: $\Phi=f_0+(A_x^3-3A_xA_y^2)f_1$, $V=V(3m)+f_4(A_y\boldsymbol{i}-A_x\boldsymbol{j})+$
$+f_5(A_x^2\boldsymbol{i}-A_y^2\boldsymbol{i}-2A_xA_y\boldsymbol{j})+(A_x^3-3A_xA_y^2)f_6\boldsymbol{k}$.

Series $\bar{6}2m$, $f=f(A_z^2,\ A_x^2+A_y^2,\ A_x^3-3A_xA_y^2)$:

Class $\bar{6}2m$ ($2\parallel X$): $\Phi=f$, $V=A_zf_1\boldsymbol{k}+f_2(A_x\boldsymbol{i}+A_y\boldsymbol{j})+$
$+f_3(A_x^2\boldsymbol{i}-A_y^2\boldsymbol{i}-2A_xA_y\boldsymbol{j})$;

Class 32 ($2\parallel X$): $\Phi=f_0+A_z(A_y^3-3A_x^2A_y)f_1$, $V=V(\bar{6}2m)+$
$+A_zf_4(A_y\boldsymbol{i}-A_x\boldsymbol{j})+A_zf_5(2A_xA_y\boldsymbol{i}+A_x^2\boldsymbol{j}-A_y^2\boldsymbol{j})+(A_y^3-3A_x^2A_y)f_6\boldsymbol{k}$;

Class $\bar{6}$: $\Phi=f_0+(A_y^3-3A_x^2A_y)f_1$, $V=V(\bar{6}2m)+f_4(A_y\boldsymbol{i}-A_x\boldsymbol{j})+$
$+f_5(2A_xA_y\boldsymbol{i}+A_x^2\boldsymbol{j}-A_y^2\boldsymbol{j})+A_z(A_y^3-3A_x^2A_y)f_6\boldsymbol{k}$.

Series $6mm$, $f=f(A_z,\ A_x^2+A_y^2,\ A_x^6-15A_x^4A_y^2+15A_x^2A_y^4-A_y^6)$:

Class $6mm$: $\Phi=f$, $V=f_1\boldsymbol{k}+f_2(A_x\boldsymbol{i}+A_y\boldsymbol{j})+$
$+(A_x^3-3A_xA_y^2)f_3(A_x^2\boldsymbol{i}-A_y^2\boldsymbol{i}-2A_xA_y\boldsymbol{j})$;

Class 6: $\Phi=f_0+(3A_x^5A_y-10A_x^3A_y^3+3A_xA_y^5)f_1$, $V=V(6mm)+$
$+f_4(A_y\boldsymbol{i}-A_x\boldsymbol{j})+(A_x^3-3A_xA_y^2)f_5(2A_xA_y\boldsymbol{i}+A_x^2\boldsymbol{j}-A_y^2\boldsymbol{j})+$
$+(3A_x^5A_y-10A_x^3A_y^3+3A_xA_y^5)f_6\boldsymbol{k}$.

Series $6/mmm$, $f=f(A_z^2,\ A_x^2+A_y^2,\ A_x^6-15A_x^4A_y^2+15A_x^2A_y^4-A_y^6)$:

Class $6/mmm$: $\Phi=f$, $V=A_zf_1\boldsymbol{k}+f_2(A_x\boldsymbol{i}+A_y\boldsymbol{j})+$
$+(A_x^3-3A_xA_y^2)f_3(A_x^2\boldsymbol{i}-A_y^2\boldsymbol{i}-2A_xA_y\boldsymbol{j})$;

Class $6/m$: $\Phi=f_0+(3A_x^5A_y-10A_x^3A_y^3+3A_xA_y^5)f_1$, $V=V(6/mmm)+$
$+f_4(A_y\boldsymbol{i}-A_x\boldsymbol{j})+(A_x^3-3A_xA_y^2)f_5(2A_xA_y\boldsymbol{i}+A_x^2\boldsymbol{j}-A_y^2\boldsymbol{j})+$
$+A_z(3A_x^5A_y-10A_x^3A_y^3+3A_xA_y^5)f_6\boldsymbol{k}$;

Class 622: $\Phi=f_0+A_z(3A_x^5A_y-10A_x^3A_y^3+3A_xA_y^5)f_1$, $V=V(6/mmm)+$
$+A_zf_4(A_y\boldsymbol{i}-A_x\boldsymbol{j})+A_z(A_x^3-3A_xA_y^2)f_5(2A_xA_y\boldsymbol{i}+A_x^2\boldsymbol{j}-A_y^2\boldsymbol{j})+$
$+(3A_x^5A_y-10A_x^3A_y^3+3A_xA_y^5)f_6\boldsymbol{k}$;

Table 87.1 (cont'd)

Class $\bar{3}m$ ($m \perp X$): $\Phi = f_0 + A_z (A_y^3 - 3A_x^2 A_y) f_1$, $V = V(6/mmm) +$

$$+ A_z f_4 (2A_x A_y \boldsymbol{i} + A_x^2 \boldsymbol{j} - A_y^2 \boldsymbol{j}) + (A_y^3 - 3A_x^2 A_y) f_5 \boldsymbol{k} +$$
$$+ A_z (A_y^3 - 3A_x^2 A_y) f_6 (A_x \boldsymbol{i} + A_y \boldsymbol{j});$$

Class $\bar{3}$: $\Phi = \Phi(6/m) + A_z (A_x^3 - 3A_x A_y^2) f_2 + A_z (A_y^3 - 3A_x^2 A_y) f_3$,

$$V = V(6/m) + (A_x^3 - 3A_x A_y^2) f_7 \boldsymbol{k} + (A_y^3 - 3A_x^2 A_y) f_8 \boldsymbol{k} +$$
$$+ A_z f_9 (2A_x A_y \boldsymbol{i} + A_x^2 \boldsymbol{j} - A_y^2 \boldsymbol{j}) + A_z f_{10} (A_x^2 \boldsymbol{i} - A_y^2 \boldsymbol{i} - 2A_x A_y \boldsymbol{j}) +$$
$$+ A_z (A_x^3 - 3A_x A_y^2) f_{11} (A_x \boldsymbol{i} + A_y \boldsymbol{i}) + A_z (A_y^3 - 3A_x^2 A_y) f_{12} (A_x \boldsymbol{i} + A_y \boldsymbol{j}).$$

Series $\bar{4}3m$, $f = f(\Sigma A_x^2,\ A_x A_y A_z,\ \Sigma A_y^2 A_z^2)$:

Class $\bar{4}3m$: $\Phi = f$, $V = f_1 \Sigma A_x \boldsymbol{i} + f_2 \Sigma A_y A_z \boldsymbol{i} + f_3 \Sigma A_x^3 \boldsymbol{i}$;

Class 23: $\Phi = f_0 + (A_x^2 - A_y^2)(A_y^2 - A_z^2)(A_z^2 - A_x^2) f_1$, $V = V(\bar{4}3m) +$

$$+ f_4 \Sigma A_x (A_y^2 - A_z^2) \boldsymbol{i} + f_5 \Sigma A_y A_z (A_y^2 - A_z^2) \boldsymbol{i} + f_6 \Sigma A_x^3 (A_y^2 - A_z^2) \boldsymbol{i}.$$

Series $m3m$, $f = f(\Sigma A_x^2,\ \Sigma A_y^2 A_z^2,\ A_x^2 A_y^2 A_z^2)$:

Class $m3m$: $\Phi = f$, $V = f_1 \Sigma A_x \boldsymbol{i} + f_2 \Sigma A_x^3 \boldsymbol{i} + A_x A_y A_z f_3 \Sigma A_y A_z \boldsymbol{i}$;

Class $m3$: $\Phi = f_0 + (A_x^2 - A_y^2)(A_y^2 - A_z^2)(A_z^2 - A_x^2) f_1$, $V = V(m3m) +$

$$+ f_4 \Sigma A_x (A_y^2 - A_z^2) \boldsymbol{i} + A_x A_y A_z f_5 \Sigma A_x (A_y^2 - A_z^2) \boldsymbol{i} +$$
$$+ [\Sigma A_x^4 (A_y^2 - A_z^2)] f_6 \Sigma A_x \boldsymbol{i};$$

Class 432: $\Phi = f_0 + A_x A_y A_z (A_x^2 - A_y^2)(A_y^2 - A_z^2)(A_z^2 - A_x^2) f_1$,

$$V = V(m3m) + f_4 \Sigma A_y A_z (A_y^2 - A_z^2) \boldsymbol{i} + A_x A_y A_z f_5 \Sigma A_x (A_y^2 - A_z^2) \boldsymbol{i} +$$
$$+ A_x A_y A_z f_6 \Sigma A_x^3 (A_y^2 - A_z^2) \boldsymbol{i}.$$

Series ∞m, $f = f(A_z,\ A_x^2 + A_y^2)$:

Class ∞m: $\Phi = f$, $V = f_1 \boldsymbol{k} + f_2 (A_x \boldsymbol{i} + A_y \boldsymbol{j})$;

Class ∞: $\Phi = f$, $V = V(\infty m) + f_3 (A_y \boldsymbol{i} - A_x \boldsymbol{j})$.

Series ∞/mm, $f = f(A_z^2,\ A_x^2 + A_y^2)$:

Class ∞/mm: $\Phi = f$, $V = A_z f_1 \boldsymbol{k} + f_2 (A_x \boldsymbol{i} + A_y \boldsymbol{j})$;

Class $\infty 2$: $\Phi = f$, $V = V(\infty/mm) + A_z f_3 (A_y \boldsymbol{i} - A_x \boldsymbol{j})$;

Class ∞/m: $\Phi = f$, $V = V(\infty/mm) + f_3 (A_y \boldsymbol{i} - A_x \boldsymbol{j})$.

Series $\infty\infty m$, $f = f(\Sigma A_x^2)$:

Classes $\infty\infty m$ and $\infty\infty$: $\Phi = f$, $V = f \Sigma A_x \boldsymbol{i}$.

Notes. 1. For abbreviation the terms already given in a preceding formula are denoted by symbols **V** ($mm2$), **V** (mmm), and so on.

2. The sign Σ in the formulas for series $\bar{4}3m$, $m3m$ and $\infty\infty m$ means summation of cyclic permutations of indices x, y, z and mutually orthogonal unit vectors $\boldsymbol{i}$, $\boldsymbol{j}$, $\boldsymbol{k}$; for example, $\Sigma A_y A_z \boldsymbol{i} = A_y A_z \boldsymbol{i} + A_z A_x \boldsymbol{j} + A_x A_y \boldsymbol{k}$.

i.e. the scalar functions of vector argument $\Phi(\boldsymbol{E})$ and tensor argument $\Phi(\sigma)$ such that

$$\boldsymbol{D}=\frac{\partial\Phi(\boldsymbol{E})}{\partial\boldsymbol{E}}, \qquad D_i=\frac{\partial\Phi(\boldsymbol{E})}{\partial E_i}; \tag{87.3}$$

$$\varepsilon=\frac{\partial\Phi(\sigma)}{\partial\sigma}, \qquad \varepsilon_\lambda=\frac{\partial\Phi(\sigma)}{\partial\sigma_\lambda}. \tag{87.4}$$

Generalizing relations $\boldsymbol{D}=\boldsymbol{D}(\boldsymbol{E})$ and $\varepsilon=\varepsilon(\sigma)$ for the case of non-linear dependences, we shall proceed from formulas (87.3) and (87.4). A vector function of a vector argument satisfying (87.3) and a tensor function of a tensor argument satisfying (87.4) are called *potential functions*. Thus, for finding out crystal-physical regularities of essentially non-linear effects, it is necessary to know the general and potential vector and tensor functions compatible with the crystals' symmetry. In this case it will suffice to specify the potential, i.e. the scalar function of a vector or a tensor argument: $\Phi(\boldsymbol{E})$ or $\Phi(\sigma)$ to define the potential vector or the tensor function.

Table 87.1 gives the forms of scalar and vector functions of a vector argument compatible with the symmetry of 32 crystallographic and 7 limit classes, and Table 87.2 gives the forms of scalar functions the argument of which is a symmetric second-rank tensor. The methods of finding these functions are complicated and we shall not discuss them*. Let us only see how the Tables are compiled and what information they can supply.

In Table 87.1 crystallographic limit classes are combined into series. Each series bears the denomination of the senior class of those it contains. All classes contained in a series have equal principal vector invariants which are listed in brackets next to the series. These principal invariants serve as the arguments of arbitrary functions f, f_0, f_1, ... For instance, the principal invariants of series $mm2$ are

$$A_z,\ A_x^2 \text{ and } A_y^2.$$

In the senior class of a series any scalar function of a vector argument, invariant with respect to its symmetry group, can be represented as a function of the principal invariants. This is written down as $\Phi=f$ and means that for class $mm2$ the general vector potential is

$$\Phi=f(A_z,\ A_x^2,\ A_y^2), \tag{87.5}$$

where f is an arbitrary function of its arguments. Thus, any vector invariant of group $mm2$ can be represented as a function of invariants A_z, A_x^2, and A_y^2.

Other classes of the series have vector invariants that cannot be reduced to the principal ones. For example, in class 2 of series $mm2$

* See Smith (1962); Sirotin (1964, 1965); Pleshakov and Sirotin (1966).

Potentials Φ (B) of the Symmetric Second-Rank Tensor B Compatible with the Symmetry of Crystals and Textures

Series $\bar{1}$, $f=f(B_{xx}, B_{yy}, B_{zz}, B_{yz}, B_{zx}, B_{xy})$:

Classes 1 and $\bar{1}$: $\Phi=f$.

Series $2/m$, $f=f(B_{xx}, B_{yy}, B_{zz}, B_{xy}, B_{xz}^2, B_{yz}^2)$:

Classes 2, m, $2/m$, $(2 \parallel Z,\ m \perp Z)$: $\Phi=f_0+B_{xz}B_{yz}f_1$.

Series mmm, $f=f(B_{xx}, B_{yy}, B_{zz}, B_{yz}^2, B_{zx}^2, B_{xy}^2)$:

Classes 222, $mm2$, mmm: $\Phi=f_0+B_{yz}B_{zx}B_{xy}f_1$.

Series $\bar{3}m$, $f=f(B_{xx}+B_{yy}, B_{zz}, B_{xx}B_{yy}-B_{xy}^2,$

$B_{yz}^2+B_{zx}^2, B_{yz}^3-3B_{xz}^2B_{yz}, B_{xx}^3+6B_{xx}^2B_{yy}+9B_{xx}B_{yy}^2-12B_{xx}B_{xy}^2)$,

$$L_1=(B_{xx}-B_{yy})B_{yz}+2B_{xy}B_{xz},$$

$$L_2=B_{xx}B_{xz}^2+B_{yy}B_{yz}^2+2B_{xz}B_{yz}B_{xy},$$

$$L_3=B_{yz}[(B_{xx}+B_{yy})^2-4(B_{yy}^2-B_{xy}^2)]+8B_{xx}B_{xy}B_{xz},$$

$$L_4=(B_{xx}-B_{yy})B_{xz}-2B_{xy}B_{yz},$$

$$L_5=3(B_{xx}-B_{yy})^2B_{xy}-4B_{xy}^3,$$

$$L_6=B_{xz}(B_{xz}^2-3B_{yz}^2),$$

$$L_7=B_{xz}[(B_{xx}+B_{yy})^2-4(B_{yy}^2-B_{xy}^2)]-8B_{xx}B_{xy}B_{yz},$$

$$L_8=(B_{xx}-B_{yy})B_{xz}B_{yz}+B_{xy}(B_{yz}^2-B_{xz}^2):$$

Classes 3 and $\bar{3}$: $\Phi=f_0+\sum_{n=1}^{8}L_nf_n+L_1^2f_9+L_2L_3f_{10}+L_1L_4f_{11}$;

Classes 32, $3m$, $\bar{3}m$: $\Phi=f_0+\sum_{n=1}^{3}L_nf_n+L_1^2f_4+L_2L_3f_5$.

Series $4/mmm$, $f=f(B_{xx}+B_{yy}, B_{zz}, B_{xx}B_{yy}, B_{xy}^2, B_{xz}^2+B_{yz}^2, B_{xz}^2B_{yz}^2)$,

$$L_1=B_{xy}B_{xz}B_{yz},$$

$$L_2=B_{xx}B_{yz}^2+B_{yy}B_{xz}^2,$$

$$L_3=B_{xy}(B_{xx}-B_{yy}),$$

$$L_4=B_{xy}(B_{xz}^2-B_{yz}^2),$$

$$L_5=B_{xz}B_{yz}(B_{xx}-B_{yy}),$$

$$L_6=B_{xz}B_{yz}(B_{xz}^2-B_{yz}^2):$$

Classes 4, $\bar{4}$, $4/m$: $\Phi = f_0 + \sum_{n=1}^{6} L_n f_n + L_1 L_2 f_7$;

Classes 422, $4mm$, $\bar{4}2m$, $4/mmm$: $\Phi = f_0 + L_1 f_1 + L_2 f_2 + L_1 L_2 f_3$.

Series $6/mmm$, $f = f\,(B_{xx} + B_{yy},\ B_{zz},\ B_{xx}B_{yy} - B_{xy}^2,\ B_{xz}^2 + B_{yz}^2,$

$B_{xx}^3 + 6B_{xx}^2 B_{yy} + 9B_{xx}B_{yy}^2 - 12B_{xx}B_{xy}^2,\ B_{xz}^6 - 6B_{xz}^4 B_{yz}^2 + 9B_{xz}^2 B_{yz}^4)$,

$L_1 = B_{xx}B_{yz}^2 + B_{yy}B_{xz}^2 - 2B_{xy}B_{xz}B_{yz}$,

$L_2 = B_{xx}\,(B_{xz}^4 + 3B_{yz}^4) + 2B_{yy}B_{xz}^2\,(B_{xz}^2 + 3B_{yz}^2) - 8B_{xy}B_{xz}^3 B_{yz}$,

$L_3 = B_{xz}^2\,[(B_{xx} + B_{yy})^2 - 4\,(B_{yy}^2 - B_{xy}^2)] -$

$- 2B_{xx}\,[(B_{xx} + 3B_{yy})\,(B_{xz}^2 + B_{yz}^2) - 4B_{xy}B_{xz}B_{yz}]$,

$L_4 = B_{xy}\,(B_{xz}^2 - B_{yz}^2) + (B_{yy} - B_{xx})\,B_{xz}B_{yz}$,

$L_5 = 3B_{xy}\,(B_{xx} - B_{yy})^2 - 4B_{xy}^3$,

$L_6 = B_{xz}B_{yz}\,[3\,(B_{xz}^2 - B_{yz}^2)^2 - 4B_{xz}^2 B_{yz}^2]$,

$L_7 = B_{xz}B_{yz}\,[(B_{xx} + B_{yy})^2 - 4\,(B_{yy}^2 - B_{xy}^2)] + 4B_{xx}B_{xy}\,(B_{yz}^2 - B_{xz}^2)$,

$L_8 = B_{xy}\,[(B_{xz}^2 + B_{yz}^2)^2 + 4B_{yz}^2\,(B_{xz}^2 - B_{yz}^2)] - 4B_{xz}^3 B_{yz}\,(B_{xx} - B_{yy})$:

Classes 6, $\bar{6}$, $6/m$: $\Phi = f_0 + \sum_{n=1}^{8} L_n f_n + L_1^2 f_9 + L_2 L_3 f_{10} + L_1 L_4 f_{11}$;

Classes 622, $6mm$, $\bar{6}m2$, $6/mmm$: $\Phi = f_0 + \sum_{n=1}^{3} L_n f_n + L_1^2 f_4 + L_2 L_3 f_5$.

Series $m3m$, $f = f\,(\Sigma B_{xx},\ \Sigma B_{yy}B_{zz},\ \Sigma B_{yz}^2,\ B_{xx}B_{yy}B_{zz},\ B_{yz}B_{zx}B_{xy},\ \Sigma B_{yz}^2 B_{zx}^2)$,

$L_1 = \Sigma B_{xx}\,(B_{xy}^2 + B_{xz}^2)$,

$L_2 = \Sigma B_{xx}B_{xy}^2 B_{xz}^2$,

$L_3 = \Sigma B_{yz}^2 B_{yy}B_{zz}$,

$L_4 = \Sigma B_{xx}\,(B_{xy}^2 - B_{xz}^2)$,

$L_5 = \Sigma B_{yy}B_{zz}\,(B_{yy} - B_{zz})$,

$L_6 = \Sigma B_{xz}^2 B_{yz}^2\,(B_{xz}^2 - B_{yz}^2)$,

$L_7 = \Sigma B_{yy}B_{zz}\,(B_{xy}^2 - B_{xz}^2)$,

$L_8 = \Sigma B_{xy}^2 B_{xz}^2\,(B_{yy} - B_{zz})$:

Table 87.2 (cont'd)

Classes 23 and $m3$: $\Phi = f_0 + \sum_{n=1}^{8} L_n f_n + L_1^2 f_9 + L_2 L_3 f_{10} + L_1 L_4 f_{11}$;

Classes 432, $\bar{4}3m$ and $m3m$: $\Phi = f_0 + \sum_{n=1}^{3} L_n f_n + L_1^2 f_4 + L_2 L_3 f_5$.

Series ∞/mm, $f = f\,(B_{xx} + B_{yy},\ B_{zz},\ B_{xx}B_{yy} - B_{xy}^2,$

$B_{xz}^2 + B_{yz}^2,\ 2B_{xy}B_{xz}B_{yz} - B_{xx}B_{yz}^2 - B_{yy}B_{xz}^2)$:

Classes ∞ and ∞/m: $\Phi = f_0 + [(B_{xx} - B_{yy})\,B_{xz}B_{yz} - B_{xy}\,(B_{xz}^2 - B_{yz}^2)]\,f_1$;

Classes $\infty 2$, ∞m and ∞/mm: $\Phi = f$.

Series $\infty\infty m$, $f = f\,(\Sigma B_{xx},\ \Sigma\,(B_{yy}B_{zz} - B_{xy}B_{xz}),$

$B_{xx}B_{yy}B_{zz} + 2B_{yz}B_{zx}B_{xy} - \Sigma B_{xx}B_{yz}^2)$:

Classes $\infty\infty$ and $\infty\infty m$: $\Phi = f$.

Note. The sign Σ in formulas for series $m3m$ and $\infty\infty m$ means summation of cyclic permutations of indices x, y, z.

such an additional invariant is $A_x A_y$. It cannot be derived from the principal invariants*, but its square is the function of the principal invariants (namely, the product of the principal invariants A_x^2 and A_y^2). Hence it follows that any function of the principal invariants and an additional invariant can be written down in the form

$$\Phi\,(A_z,\ A_x^2,\ A_y^2,\ A_x A_y) = f_0\,(A_z,\ A_x^2,\ A_y^2) + A_x A_y f_1\,(A_z,\ A_x^2,\ A_y^2); \tag{87.6}$$

this is represented in the Table in the form

$$\Phi = f_0 + A_x A_y f_1.$$

The essential advantage of this notation is its unambiguity. Indeed, functions f_0 and f_1 are uniquely determined from function Φ. The function f_0 is an even component of function Φ with respect

* It may seem that it is equal to the square root of the product of the second and third principal invariants, but it is not so: $\sqrt{A_x^2 A_y^2} = |A_x A_y|$.

to A_xA_y, while $A_xA_yf_1$ is an odd component, therefore

$$f_0 = -\frac{1}{2}[\Phi(A_z, A_x^2, A_y^2; A_xA_y) + \Phi(A_z, A_x^2, A_y^2; -A_xA_y)],$$

$$f_1 = \frac{1}{2A_xA_y}[\Phi(A_z, A_x^2, A_y^2; A_xA_y) - \Phi(A_z, A_x^2, A_y^2; -A_xA_y)].$$

According to Table 87.1 the general vector function for class $mm2$ has the form

$$V = A_xf_1\boldsymbol{i} + A_yf_2\boldsymbol{j} + f_3\boldsymbol{k}, \tag{87.7}$$

while the potential function, as it follows from (87.3) and (87.5) has the form

$$V = \frac{\partial f}{\partial A_x}\boldsymbol{i} + \frac{\partial f}{\partial A_y}\boldsymbol{j} + \frac{\partial f}{\partial A_z}\boldsymbol{k}, \tag{87.8}$$

where f_1, f_2, f_3 and f are arbitrary functions of the principal invariants A_z, A_x^2, and A_y^2. As for class 2, the general vector function has the form*

$$V = (A_xf_1 + A_yf_2)\,\boldsymbol{i} + (A_xf_3 + A_yf_4)\,\boldsymbol{j} + (f_5 + A_xA_yf_6)\,\boldsymbol{k}, \tag{87.9}$$

and the potential function has the form

$$V = \frac{\partial\Phi}{\partial A_x}\boldsymbol{i} + \frac{\partial\Phi}{\partial A_y}\boldsymbol{j} + \frac{\partial\Phi}{\partial A_z}\boldsymbol{k}, \tag{87.10}$$

where $\Phi = f_0 + A_xA_yf_1$; all f_α are the functions of the principal invariants**.

As was already noted, Tables 87.1 and 87.2 give the forms of the most general functional dependences compatible with the crystal's symmetry. But among all possible scalar, vector and tensor functions of the vector and tensor arguments an especially important place is occupied by integral rational functions, i.e. such whose components are polynomials of the argument components***.

Let us again return to Table 87.1. Let us select as an example class $\bar{4}2m$ of series $4/mmm$. We shall consider general and potential vector functions which would be integral rational functions of the fourth degree.

As it follows from Table 87.1, the general vector function $V = V(A)$, compatible with the crystal's symmetry, has the form

$$V = (A_zf_1 + A_xA_yf_2)\,\boldsymbol{k} + (f_3 + A_xA_yA_zf_4)(A_x\boldsymbol{i} + A_y\boldsymbol{j}) + (A_zf_5 + A_xA_yf_6)(A_y\boldsymbol{i} + A_x\boldsymbol{j}). \tag{87.11}$$

* Some of the terms in the Table are denoted by V ($mm2$) for brevity. All the terms are written down in their explicit form, and the arbitrary functions f_α are numbered. We want to emphasize that function f_1 does not coincide with the function of the same denomination in (87.6).

** The enumeration of functions f in the expressions for Φ and V is independent, therefore no significance is to be attributed to the coincidence of the function numbers in these expressions.

*** See Döring (1958); Smith (1970); Smith, Smith and Rivlin (1963); Smith and Rivlin (1964); Smith and Kiral (1969).

In order to have in the components V_i all necessary terms up to those of the fourth degree inclusive with respect to the components A_k functions f_α must include all terms up to the degrees

Function	f_1	f_2	f_3	f_4	f_5	f_6
Degree	3	2	3	0	2	1

In this case $A_x^2 + A_y^2$, A_z^2 and $A_x^2 A_y^2$ serve as the principal invariants. Since they all have an even power with respect to A, the terms of odd powers in functions f_α are identically zero.

The general forms of functions f_α are

$$\begin{aligned} f_1 &= a_1 + c_1 (A_x^2 + A_y^2) + c_2 A_z^2, \\ f_2 &= b_1 + d_1 (A_x^2 + A_y^2) + d_2 A_z^2, \\ f_3 &= a_2 + c_3 (A_x^2 + A_y^2) + c_4 A_z^2, \\ f_4 &= d_3, \\ f_5 &= b_2 + d_4 (A_x^2 + A_y^2) + d_5 A_z^2, \\ f_6 &= c_5, \end{aligned} \tag{87.12}$$

where $a_1, \ldots, d_5$ are certain constants. The components of vector-function $V(A)$ compatible with the symmetry of class $\bar{4}2m$ are the coefficients of mutually orthogonal unit vectors $\boldsymbol{i}$, $\boldsymbol{j}$ and $\boldsymbol{k}$ respectively:

$$\begin{aligned} V_x &= A_x f_3 + A_x^2 A_y A_z f_4 + A_y A_z f_5 + A_x A_y^2 f_6, \\ V_y &= A_y f_3 + A_x A_y^2 A_z f_4 + A_x A_z f_5 + A_x^2 A_y f_6, \\ V_z &= A_z f_1 + A_x A_y f_2. \end{aligned} \tag{87.13}$$

Substituting into these formulas the expansions of functions f_α given in (87.12), we obtain

$$\begin{aligned} V_x &= a_2 A_x + b_2 A_y A_z + c_3 A_x (A_x^2 + A_y^2) + c_4 A_x A_z^2 + \\ &\quad + c_5 A_x A_y^2 + d_3 A_x^2 A_y A_z + d_4 (A_x^2 + A_y^2) A_y A_z + d_5 A_y A_z^3, \\ V_y &= a_2 A_y + b_2 A_x A_z + c_3 A_y (A_x^2 + A_y^2) + c_4 A_y A_z^2 + \\ &\quad + c_5 A_x^2 A_y + d_3 A_x A_y^2 A_z + d_4 A_x (A_x^2 + A_y^2) A_z + d_5 A_x A_z^3, \\ V_z &= a_1 A_z + b_1 A_x A_y + c_1 (A_x^2 + A_y^2) A_z + c_2 A_z^3 + \\ &\quad + d_1 A_x A_y (A_x^2 + A_y^2) + d_2 A_x A_y A_z^2. \end{aligned} \tag{87.14}$$

Such is the general integral rational vector function of the fourth degree compatible with the symmetry of crystals of class $\bar{4}2m$.

Now let us construct a potential vector function of the same power. For this purpose it is necessary to write the potential up to terms of the fifth degree inclusive. According to Table 87.1 the potential for class $\bar{4}2m$ is

$$\Phi = f_0 + A_x A_y A_z f_1. \tag{87.15}$$

So that we could obtain all the terms we are interested in, function f_0 should be written up to terms of the fourth degree, and function f_1, up to terms of the second degree inclusive:

$$f_0 = h_1 + l_1 (A_x^2 + A_y^2) + l_2 A_z^2 + n_1 A_x^2 A_y^2 + \\ + n_2 (A_x^2 + A_y^2)^2 + n_3 (A_x^2 + A_y^2) A_z^2 + n_4 A_z^4, \qquad (87.16)$$

$$f_1 = m_1 + p_1 (A_x^2 + A_y^2) + p_2 A_z^2.$$

Substituting these expressions into (87.15), we obtain the potential

$$\Phi = h_1 + l_1 (A_x^2 + A_y^2) + l_2 A_z^2 + m A_x A_y A_z + n_1 A_x^2 A_y^2 + n_2 (A_x^2 + A_y^2)^2 + \\ + n_3 (A_x^2 + A_y^2) A_z^2 + n_4 A_z^4 + p_1 A_x A_y (A_x^2 + A_y^2) A_z + p_2 A_x A_y A_z^2. \qquad (87.17)$$

The derivatives of the potential are equal to the components of the potential vector function:

$$V_x = \frac{\partial \Phi}{\partial A_x} = 2 l_1 A_x + m_1 A_y A_z + 2 n_1 A_x A_y^2 + 4 n_2 A_x (A_x^2 + A_y^2) + \\ + 2 n_3 A_x A_z^2 + p_1 (3 A_x^2 + A_y^2) A_y A_z + p_2 A_y A_z^3,$$

$$V_y = \frac{\partial \Phi}{\partial A_y} = 2 l_1 A_y + m_1 A_x A_z + 2 n_1 A_x^2 A_y + 4 n_2 A_y (A_x^2 + A_y^2) + \\ + 2 n_3 A_y A_z^2 + p_1 A_x (A_x^2 + 3 A_y^2) A_z + p_2 A_x A_z^3, \qquad (87.18)$$

$$V_z = \frac{\partial \Phi}{\partial A_z} = 2 l_2 A_z + m_1 A_x A_y + 2 n_3 (A_x^2 + A_y^2) A_z + 4 n_3 A_z^3 + \\ + p_1 A_x A_y (A_x^2 + A_y^2) + 3 p_2 A_x A_y A_z^2.$$

While the general vector function of the fourth degree compatible with the symmetry of crystals of class $\bar{4}2m$ is determined by fourteen constant coefficients, the similar potential function is determined by only nine coefficients. Therefore, for the vector function of symmetry $\bar{4}2m$ of the fourth degree to be potential, its coefficients must satisfy five conditions. We shall easily find these conditions by comparing formulas (87.14) and (87.18):

$$b_1 = b_2, \qquad c_1 = c_4, \\ 2 d_1 = d_3 = 2 d_4, \qquad d_2 = 3 d_5. \qquad (87.19)$$

Integral rational vector functions are closely connected with tensor expansions of the form (87.1). Let us consider such an expansion of vector function $V(A)$:

$$V_i = T_i^{(1)} + T_{ij}^{(2)} A_j + T_{ijk}^{(3)} A_j A_k + T_{ijkl}^{(4)} A_i A_k A_l + T_{ijklm}^{(5)} A_j A_k A_l A_m. \qquad (87.20)$$

Here tensors $\mathbf{T}^{(1)}, \ldots, \mathbf{T}^{(5)}$ play the role of matter tensors. The internal symmetry of all tensors is $V[V^{n-1}]$—they are symmetric

with respect to all indices, except the first one. Their components can be calculated by differentiating function $V(A)$ at point $A = 0$, namely:

$$T_i^{(1)} = (V_i)_{A=0}, \qquad T_{ij}^{(2)} = \left(\frac{\partial V_i}{\partial A_j}\right)_{A=0},$$

$$T_{ijk}^{(3)} = \frac{1}{2}\left(\frac{\partial^2 V_i}{\partial A_j \partial A_k}\right)_{A=0}, \qquad T_{ijkl}^{(4)} = \frac{1}{3!}\left(\frac{\partial^3 V_i}{\partial A_j \partial A_k \partial A_l}\right)_{A=0}, \tag{87.21}$$

$$T_{ijklm}^{(5)} = \frac{1}{4!}\left(\frac{\partial^4 V_i}{\partial A_j \partial A_k \partial A_l \partial A_m}\right)_{A=0}.$$

Evidently, in case of any n

$$T_{i_1 \ldots i_n}^{(n)} = \frac{1}{(n-1)!}\left(\frac{\partial^{n-1} V_{i_1}}{\partial A_{i_2} \ldots \partial A_{i_n}}\right)_{A=0}. \tag{87.22}$$

By means of these formulas it is possible to find the components of tensors $\mathbf{T}^{(n)}$, invariant with respect to the specified point groups, in terms of integral rational vector functions constructed with the aid of Table 87.1. For instance, with the aid of expansion (87.14) we can find the components of tensors $\mathbf{T}^{(n)}$ invariant with respect to group $\bar{4}2m$. Let us do it.

Obviously

$$T_i^{(1)} = 0 \quad (i = 1,\ 2,\ 3). \tag{87.23}$$

This is not to be wondered at: $\bar{4}2m$ is not a pyroelectric class.

Let us find the components of tensor $\mathbf{T}^{(2)}$. The non-zero ones among them are only*

$$T_{11} = \frac{\partial V_x}{\partial A_x} = a_2, \quad T_{22} = \frac{\partial V_y}{\partial A_y} = a_2, \quad T_{33} = \frac{\partial V_z}{\partial A_z} = a_1. \tag{87.24}$$

As was to be expected, all non-diagonal components are zero and $T_{11} = T_{22}$.

Let us next find the components of tensor $\mathbf{T}^{(3)}$; its internal symmetry is $V[V^2]$. The non-zero components are the following:

$$\begin{aligned} T_{123} &= T_{132} = \frac{1}{2}\frac{\partial^2 V_x}{\partial A_y \partial A_z} = \frac{1}{2} b_2, \\ T_{231} &= T_{213} = \frac{1}{2}\frac{\partial^2 V_y}{\partial A_z \partial A_x} = \frac{1}{2} b_2, \\ T_{312} &= T_{321} = \frac{1}{2}\frac{\partial^2 V_z}{\partial A_x \partial A_y} = \frac{1}{2} b_1. \end{aligned} \tag{87.25}$$

Thus we have obtained the components of the tensor of piezoelectric (or electrooptical) coefficients for class $\bar{4}2m$.

* To obtain the customary notation for tensor components their letter indices are replaced by digital ones.

Finally, tensor $\mathbf{T}^{(4)}$ has the following non-zero components:

$$
\begin{aligned}
&T_{1111}=\frac{1}{6}\frac{\partial^3 V_x}{\partial A_x^3}=c_3,\\
&T_{1122}=T_{1212}=T_{1221}=\frac{1}{6}\frac{\partial^3 V_x}{\partial A_x \partial A_y^2}=\frac{1}{3}(c_3+c_5),\\
&T_{1133}=T_{1313}=T_{1331}=\frac{1}{6}\frac{\partial^3 V_x}{\partial A_x \partial A_z^2}=\frac{1}{3}c_4,\\
&T_{2112}=T_{2121}=T_{2211}=\frac{1}{6}\frac{\partial^3 V_y}{\partial A_x^2 \partial A_y}=\frac{1}{3}(c_3+c_5),\\
&T_{2222}=\frac{1}{6}\frac{\partial^3 V_y}{\partial A_y^3}=c_3,\\
&T_{2233}=T_{2323}=T_{2332}=\frac{1}{6}\frac{\partial^3 V_y}{\partial A_y \partial A_z^2}=\frac{1}{3}c_4,\\
&T_{3113}=T_{3131}=T_{3311}=\frac{1}{6}\frac{\partial^3 V_z}{\partial A_x^2 \partial A_z}=\frac{1}{3}c_1,\\
&T_{3223}=T_{3232}=T_{3322}=\frac{1}{6}\frac{\partial^3 V_z}{\partial A_y^2 \partial A_z}=\frac{1}{3}c_1,\\
&T_{3333}=\frac{1}{6}\frac{\partial^3 V_z}{\partial A_z^3}=c_2.
\end{aligned}
\tag{87.26}
$$

The internal symmetry of this tensor is $V\,[V^3]$. It can describe, for example, cubic polarizability and, correspondingly, the generation of a third light harmonic in crystals of classes 422, $4mm$, $\bar{4}2mm$ and $4/mmm$ (as this tensor is of the even type, it has the same form for all classes of one subsystem).

The calculation of tensor $\mathbf{T}^{(5)}$ with internal symmetry $V\,[V^4]$ is left for the reader.

The potential integral rational vector functions are quite similarly used for the construction of tensors symmetric with respect to all indices.

Thus, Table 87.1 makes it possible to write down without any trouble tensors of not simply a high rank but of an arbitrarily high rank invariant with respect to any specified group. But integral rational vector functions can also be used directly instead of matter tensors of high ranks. The notation of the properties of a material with the aid of these functions will be somewhat more compact than with the aid of matter tensors; indeed, formulas (87.14) or (87.18) take much less space than would be required for four tensors of the second, third, fourth and fifth ranks respectively containing the same information. Thus we have come to an essential generalization

of the concept of matter tensors—to the idea of material vector or tensor functions*.

Table 87.2 contains the potentials of a symmetric second-rank tensor compatible with the symmetry of crystals and textures. The general tensor functions of such type have not yet been constructed. The form of the potential is the same for all classes of one subsystem. The subsystems are combined into series; in this case series coincide with systems.

With the aid of these potentials the generalization of Hooke's law is easily obtained in the form

$$\varepsilon_\lambda = \frac{\partial \Phi(\sigma)}{\partial \sigma_\lambda}, \tag{87.27}$$

or in the form

$$\sigma_\lambda = \frac{\partial \Phi(\varepsilon)}{\partial \varepsilon_\lambda}. \tag{87.28}$$

Of course it is necessary to bear in mind the recalculation rules

$$\sigma_\lambda = \sigma_{ij} \qquad (ij \leftrightarrow \lambda = 1, \ldots, 6), \tag{87.29}$$

$$\varepsilon_\lambda = \begin{cases} \varepsilon_{ij} & (ij \leftrightarrow \lambda = 1, 2, 3), \\ 2\varepsilon_{ij} & (ij \leftrightarrow \lambda = 4, 5, 6); \end{cases} \tag{87.30}$$

for instance, writing down potential $\Phi(\varepsilon) = \Phi(\varepsilon_1, \ldots, \varepsilon_6)$, ε_1 should be written instead of B_{xx} but instead of B_{xy} there must be substituted $1/2\varepsilon_6$.

The written out tensor potentials can also be used for finding the form of tensors characterizing the corrections to Hooke's law, i.e. tensors $s^{(2)}$, $s^{(3)}$, ... in expansion (87.2) and tensors $c^{(2)}$, $c^{(3)}$, ... in the expansion

$$\sigma_\lambda = c^{(1)}_{\lambda\mu}\varepsilon_\mu + c^{(2)}_{\lambda\mu\nu}\varepsilon_\mu\varepsilon_\nu + c^{(3)}_{\lambda\mu\nu\varkappa}\varepsilon_\mu\varepsilon_\nu\varepsilon_\varkappa + \ldots \tag{87.31}$$

for crystals of any class (more exactly, of any subsystem). It is exactly for determining the coefficients $s^{(2)}_{\lambda\mu\nu}$ and $c^{(2)}_{\lambda\mu\nu}$ that we need the potentials representing polynomials of the third degree with respect to tensor components, while for calculating coefficients $s^{(3)}_{\lambda\mu\nu\varkappa}$ and $c^{(3)}_{\lambda\mu\nu\varkappa}$ polynomials of the fourth degree are required.

* Such functions are used, in particular, in the mathematical apparatus of the theory of phase transitions of the second kind, expressing the general form of the dependence of thermodynamic potential Φ on the parameter of dissymmetry $\boldsymbol{c}$ (see Sec. 66). For two- and three-dimensional vectors $\boldsymbol{c}$ Table 87.1 will suffice (Sirotin, 1967; Sirotin and Michelson, 1969), but for multidimensional vectors $\boldsymbol{c}$ it is necessary to resort to special mathematical methods (Gufan and Sakhnenko, 1972).

For example, potential $\Phi(\sigma)$ for crystals of the senior subsystem of the cubic system, up to terms of the third degree, is equal to

$$\Phi(\sigma) = a(\sigma_1 + \sigma_3 + \sigma_3) + b_1(\sigma_1 + \sigma_2 + \sigma_3)^2 + b_2(\sigma_2\sigma_3 + \sigma_3\sigma_1 + \sigma_1\sigma_2) + \\ + b_3(\sigma_4^2 + \sigma_5^2 + \sigma_6^2) + d_1(\sigma_1 + \sigma_2 + \sigma_3)^3 + d_2(\sigma_1 + \sigma_2 + \sigma_3) \times \\ \times (\sigma_2\sigma_3 + \sigma_3\sigma_1 + \sigma_1\sigma_2) + d_3(\sigma_1 + \sigma_2 + \sigma_3)(\sigma_4^2 + \sigma_5^2 + \sigma_6^2) + \\ + d_4\sigma_1\sigma_2\sigma_3 + d_5\sigma_4\sigma_5\sigma_6 + d_6(\sigma_1\sigma_5^2 + \sigma_1\sigma_6^2 + \sigma_2\sigma_6^2 + \sigma_2\sigma_4^2 + \sigma_3\sigma_4^2 + \sigma_3\sigma_5^2). \tag{87.32}$$

Evidently,

$$s_{\lambda\mu\nu}^{(2)} = \frac{1}{2}\frac{\partial^3\Phi}{\partial\sigma_\lambda\partial\sigma_\mu\partial\sigma_\nu}; \tag{87.33}$$

thus, elastic compliance coefficients of the second order

$$\begin{aligned} &s_{111} = s_{222} = s_{333} = 3d_1, \\ &s_{122} = s_{133} = s_{233} = s_{211} = s_{311} = s_{322} = 3d_1 + d_2; \\ &s_{123} = 3d_1 + \frac{3}{2}d_2 + \frac{1}{2}d_4, \\ &s_{144} = s_{255} = s_{366} = d_3, \\ &s_{155} = s_{166} = s_{266} = s_{244} = s_{344} = s_{355} = d_3 + d_6, \\ &s_{456} = \frac{1}{2}d_5; \end{aligned} \tag{87.34}$$

the other coefficients (except those differing from the ones written out only by permutations of indices) are zero. However, even in this case it is more convenient to obtain, by differentiating the potential, formulas directly expressing strains in terms of stresses:

$$\varepsilon_1 = a + 2b_1\sigma_1 + (2b_1 + b_2)(\sigma_2 + \sigma_3) + 3d_1\sigma_1^2 + (6d_1 + 2d_2)\sigma_1(\sigma_2 + \sigma_3) + \\ + (3d_1 + d_2)(\sigma_2^2 + \sigma_3^2) + (6d_1 + 3d_2 + d_4)\sigma_2\sigma_3 + d_3\sigma_4^2 + d_6(\sigma_5^2 + \sigma_6^2), \tag{87.35}$$

$$\varepsilon_4 = 2b_3\sigma_4 + 2d_3\sigma_1\sigma_4 + (2d_3 + 2d_6)(\sigma_2 + \sigma_3)\sigma_4 + d_5\sigma_5\sigma_6;$$

formulas for the other components differ from those written down only by cyclic permutations of indices.

APPENDICES

A. CRYSTALLOGRAPHIC AND CRYSTAL-PHYSICAL SYSTEMS OF COORDINATES

Here we have collected the rules for the choice of crystallographic and crystal-physical systems of coordinates for the crystals of all classes (see Secs. 4, 16, 86). Table A.1 gives standard stereographic projections showing the mutual array of the elements of crystal symmetry, of the crystallographic and crystal-physical coordinate axes (J. F. Nye, 1957, Appendix 2).

Table A.2 gives the rules for the choice of the standard crystallographic* and crystal-physical systems of coordinates for all 32 classes, and the rules for the choice of the right-handed modifications in 11 enantiomorphous classes. All the rules are formulated as closely as possible to the IRE Standards (1949). They were discussed in detail in Sec. 86 of this book.

Notation.

X, Y, Z are the axes of the crystallographic system of coordinates.

X_1, X_2, X_3 are the axes of the crystal-physical system of coordinates.

α, β, γ are the angles between positive directions of axes Y and Z, Z and X, X and Y respectively.

cr or cr_1 means that the given crystallographic axis is directed along the shortest lattice vector; cr_2 means a similar direction not collinear with the first one; cr_3 means a similar direction not coplanar with the first two; $\perp Y cr_1$ means that the given axis is directed along the shortest of the lattice vectors perpendicular to axis Y; other notation can be understood by analogy.

$s_{\lambda\mu}$ are the coefficients of elastic compliance, $d_{i\lambda}$ are the piezoelectric coefficients, $\pi_{\lambda\mu}$ are the piezooptic coefficients, G is the coefficient of gyration.

Both the crystallographic and crystal-physical systems are right-handed, the angles between their corresponding axes (X and X_1, Y and X_2, Z and X_3) are less than 90°. Enantiomorphous modifications are arrayed with respect to the introduced coordinate frames so that in case of inversion one of them transforms into the other.

In Section "Possible Changes" it is pointed out how the rules for the choice of coordinate axes and enantiomorphous modifications will change if crystals of the monoclinic system and class $\bar{6}m2$ are oriented differently; in the new orientation the latter class will be naturally denoted $\bar{6}2m$.

B. BRAVAIS LATTICES AND CRYSTALLOGRAPHIC MATRICES

The division of the Bravais lattices into primitive and centred ones is to a certain extent conditional. Those six lattices are considered to be primitive on whose base vectors the crystallographic systems of coordinates are usually constructed. The parameters of these lattices and their crystallographic matrices are defined by the rules for the choice of crystallographic systems of coordinates (see Appendix A). The other eight Bravais lattices are considered to be centred; for example, the rhombohedral lattice is regarded as a centred hexagonal one.

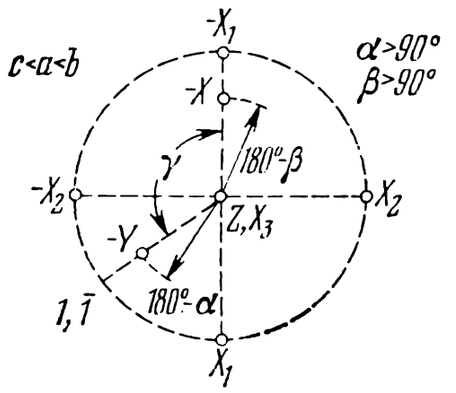
---

* On the choice of crystallographic coordinate systems in crystals of triclinic and monoclinic systems see also Delone, Padurov, Alexandrov (1934); Delone, Galiulin, Shtogrin (1974).

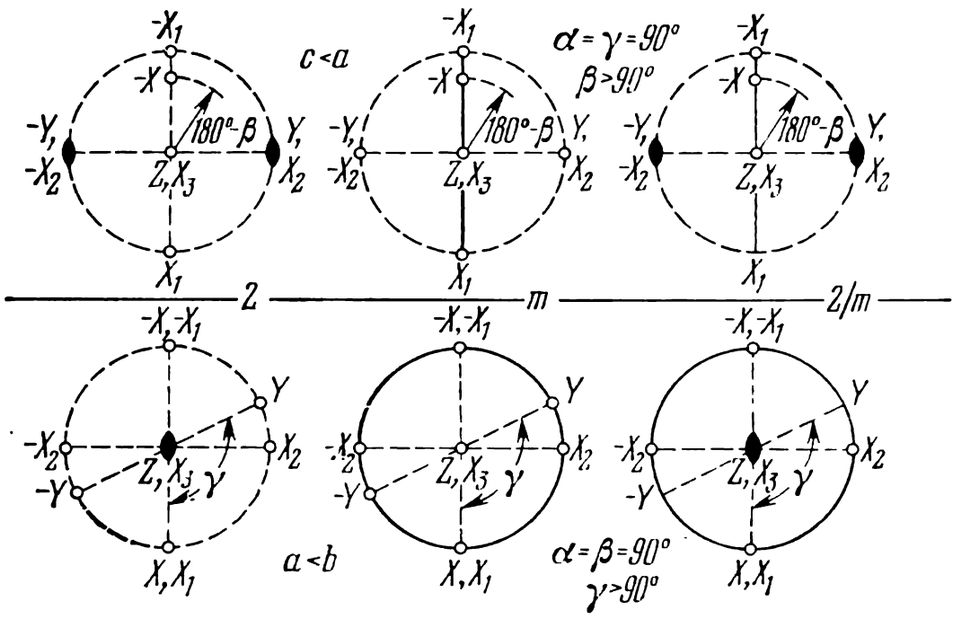
Table A.1

Choice of the Crystallographic and Crystal-Physical Coordinate Axes in Crystals of 32 Classes
(stereographic projections)

Triclinic system



Monoclinic system
(the upper row shows the conventional orientation, the lower row, the changed one)



Rhombic system

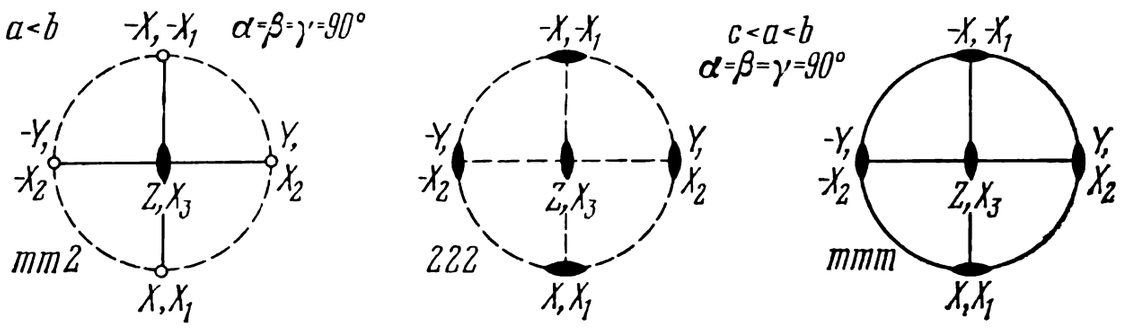
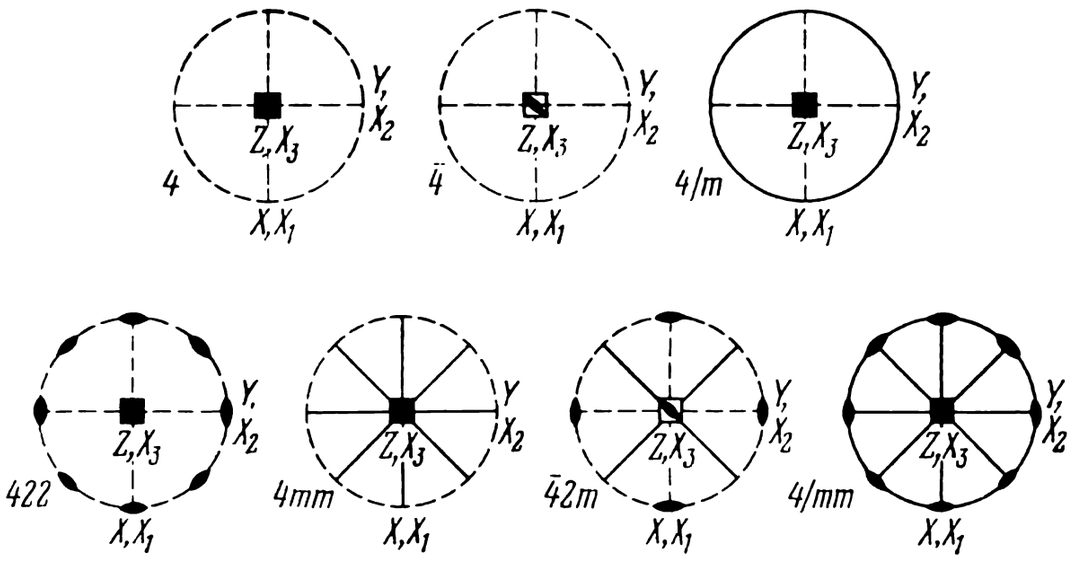


Table A.1 (cont'd)

Tetragonal system

$a=b\neq c,\ \alpha=\beta=\gamma=90°$



Hexagonal system, trigonal system

$a=b\ ,\quad \alpha=\beta=90°,\quad \gamma=120°$

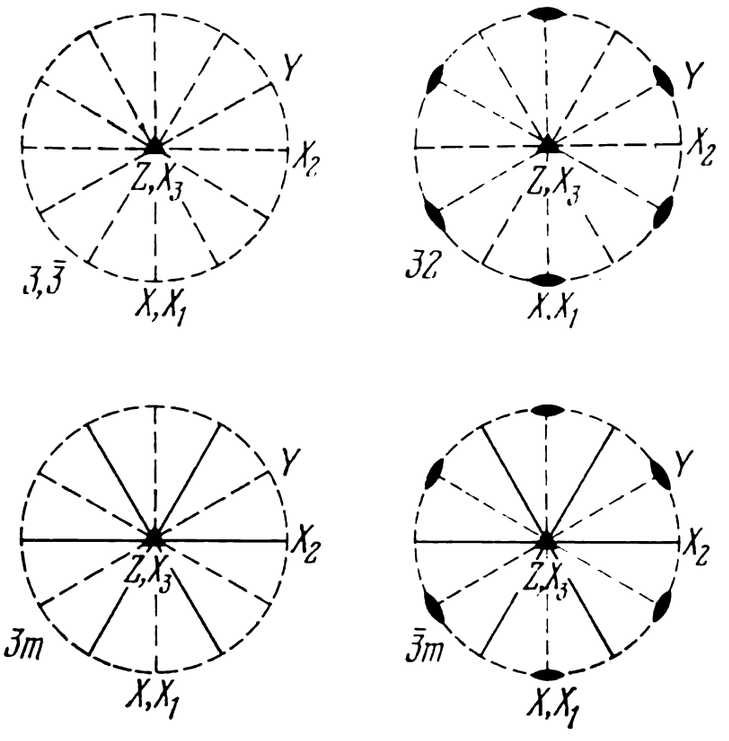


Table A.1 (cont'd)

Hexagonal system

$a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$

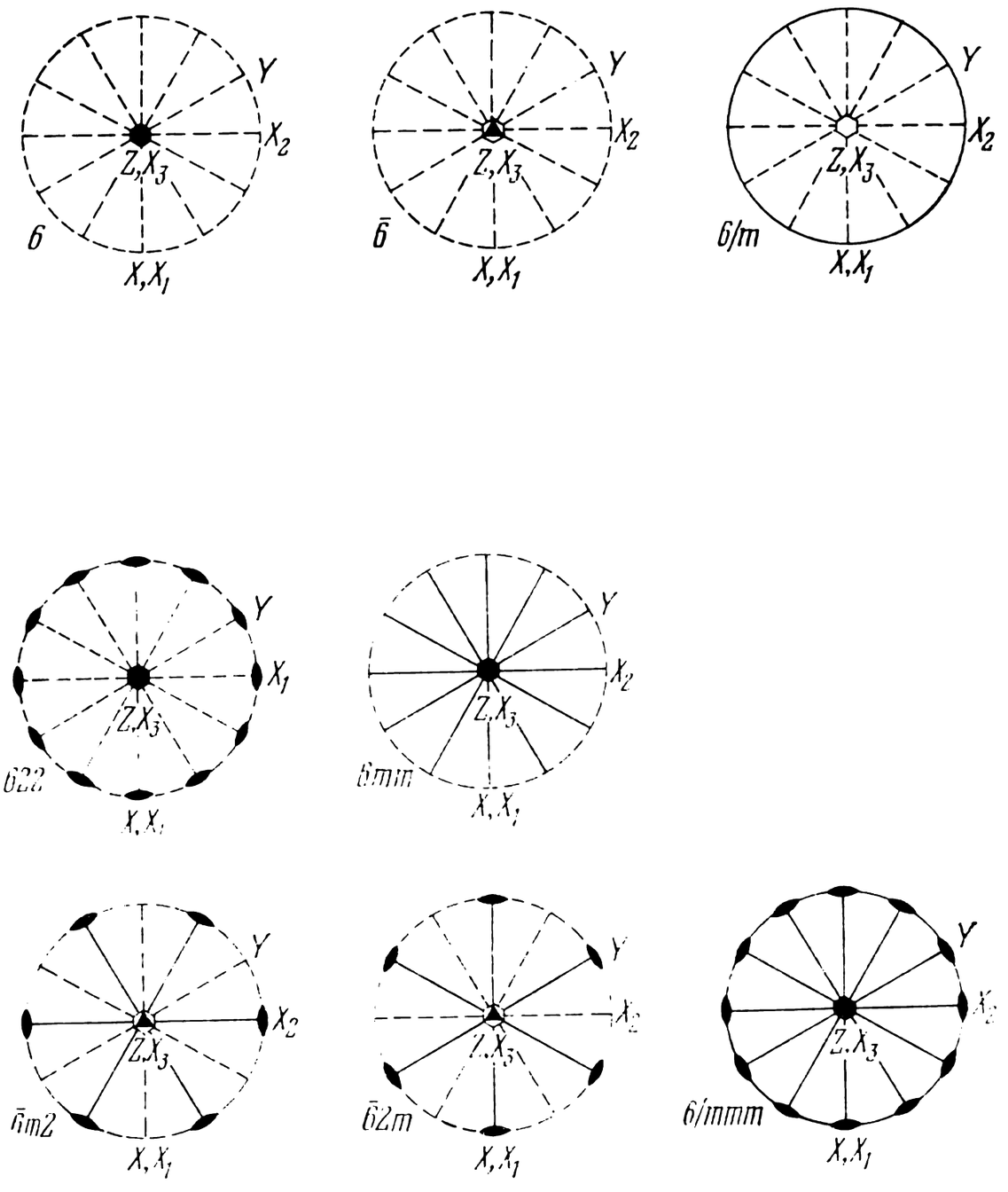
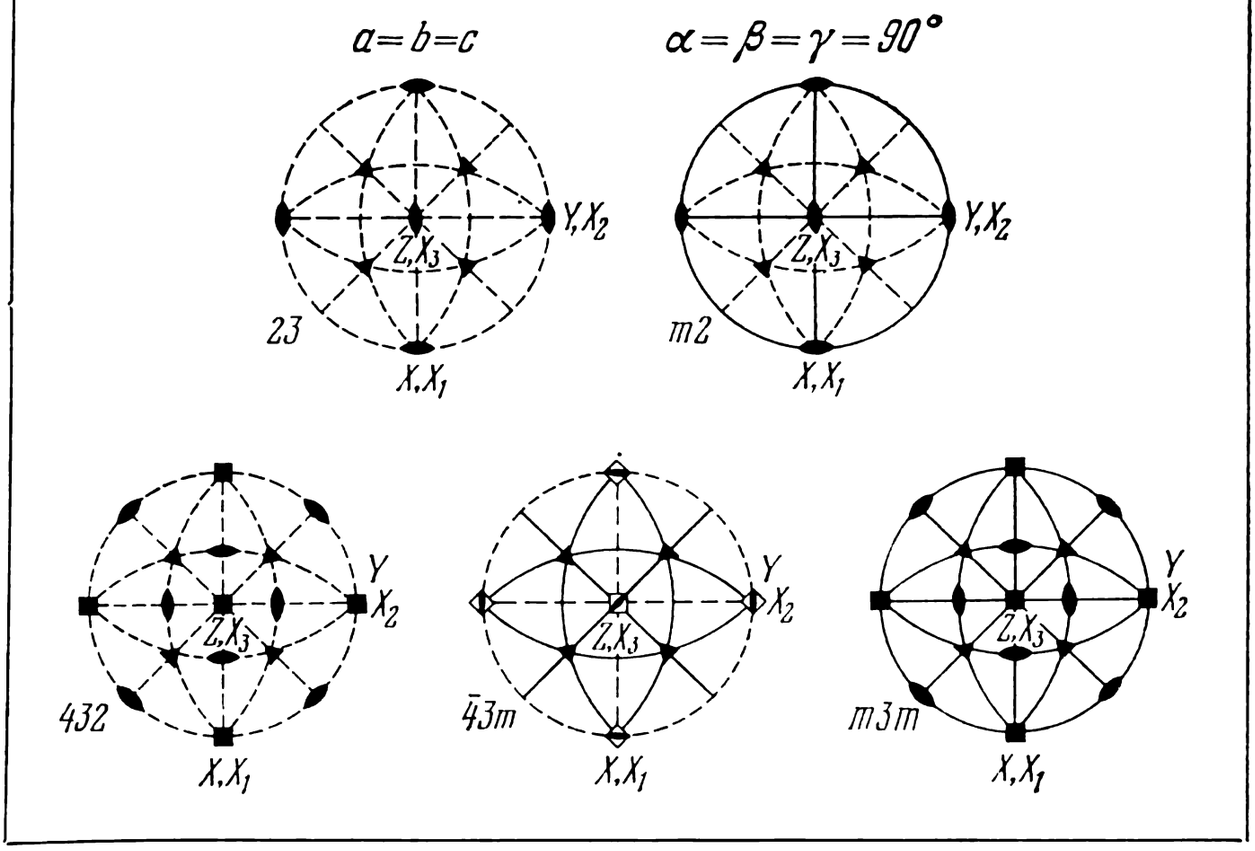


Table A.1 (cont'd)

Cubic system



Notation.

a, b, c are the lengths of the base vectors of a crystal lattice;

α, β, γ are the angles between them;

$v = abc\omega$ is the volume of a unit cell;

a^*, b^*, c^* are the lengths of the base vectors of a reciprocal lattice;

α^*, β^*, γ^* are the angles between them;

ω—see below;

$A = \| A_{\alpha i} \|$ is the matrix of the expansion of vectorial basis $\boldsymbol{a}_\alpha$ of a crystal lattice with respect to mutually orthogonal unit vectors $\boldsymbol{e}_i$ of the crystal-physical system of coordinates (Greek indices enumerate rows, Latin indices enumerate columns);

$E = \| E_i^\alpha \|$ is the matrix of the expansion of mutually orthogonal unit vectors of the crystal-physical system of coordinates with respect to base vectors $\boldsymbol{a}_\alpha$ of the crystal lattice (Latin indices enumerate rows, Greek indices enumerate columns);

$G = \| g_{\alpha\beta} \|$ is the matrix of covariant components of a metric tensor;

$G^{-1} = \| g^{\alpha\beta} \|$ is the matrix of contravariant components of a metric tensor;

$Q = \| Q_\alpha^{\beta'} \|$ is the matrix of the expansion of vectorial basis of a centred crystal lattice with respect to the base vectors of a corresponding primitive lattice (the unprimed indices are related to the centred lattice and enumerate rows, the primed ones are related to the primitive lattice and enumerate columns);

$P = \| P_{\alpha'}^\beta \|$ is the matrix of the expansion of vectorial basis of a primitive crystal lattice with respect to the base vectors of a centred lattice (the primed

Table A.2

Conventions for the Choice of Coordinate Systems and Right-Hand Modifications in 32 Crystallographic Classes

Class	Z [001]	X [100]	Y [010]	α, β, γ	X_3	X_1	X_2	Choice of coordinate system	Right-hand modification
				Triclinic system					
1	cr_1	cr_2	cr_3	$\alpha > 90°$, $\beta > 90°$	[001]	b (010)	$\perp$ (010)		$d_{33} > 0$
$\bar{1}$	cr_1	cr_2	cr_3						
				Monoclinic system					
2	$\perp Y\ cr_1$	$\perp Y\ cr_2$	$\parallel 2$	$\alpha = \gamma = 90°$, $\beta > 90°$	[001]	$\perp$ (100)	[010]		$d_{22} > 0$
m	$\perp Y\ cr_1$	$\perp Y\ cr_2$	$\perp m$					$d_{33} > 0$	
$2/m$	$\perp Y\ cr_1$	$\perp Y\ cr_2$	$\parallel 2$						
				Rhombic system					
222	$\parallel 2\ cr_1$	$\parallel 2\ cr_2$	$\parallel 2cr_3$	$\alpha = \beta = \gamma = 90°$	[001]	[100]	[010]		$d_{36} > 0$
$mm2$	$\parallel 2$	$\perp Z\ cr_1$	$\perp mcr_2$					$d_{33} > 0$	
mmm	$\parallel 2\ cr_1$	$\parallel 2\ cr_2$	$\parallel 2\ cr_3$						

Table A.2 (cont'd)

Class	Z [001]	X [100]	Y [010]	α, β, γ	X_3	X_1	X_2	Choice of coordinate system	Right-hand modification
				Tetragonal system					
4	∥ 4	⊥ Z cr		$\alpha=\beta=\gamma=90°$	[001]	[100]	[010]	$s_{16}>0$	$d_{33}>0$
$\bar{4}$	∥ $\bar{4}$	⊥ Z cr						$s_{16}>0$ $d_{36}>0$	
4/m	∥ 4	⊥ Z cr						$s_{16}>0$	
422	∥ 4	⊥ Z cr							$d_{14}>0$
4mm	∥ 4	⊥ Z cr						$d_{33}>0$	
$\bar{4}2m$	∥ $\bar{4}$	∥ 2						$d_{33}>0$	
4/mmm	∥ 4	⊥ Z cr							
				Hexagonal system					
3	∥ 3	⊥ Z cr						$s_{14}>0$, $s_{25}>0$	$d_{33}>0$
$\bar{3}$	∥ 3	⊥ Z cr						$s_{14}>0$, $s_{25}>0$	
32	∥ 3	∥ 2						$s_{14}>0$	$d_{11}>0$

Table A.2 (cont'd)

Class	Z [001]	X [100]	Y [010]	α, β, γ	X_3	X_1	X_2	Choice of coordinate system	Right-hand modification
				Hexagonal system					
$3m$	∥ 3	⊥ m						$s_{14} > 0$ $d_{33} > 0$	
$\bar{3}m$	∥ 3	∥ 2						$s_{14} > 0$	
6	∥ 6	⊥ Z cr		$\alpha = \beta = \gamma = 90°$, $\gamma = 120°$	[0001]	$[2\bar{1}\bar{1}0]$	$[01\bar{1}0]$		$d_{33} > 0$
$\bar{6}$	∥ $\bar{6}$	⊥ Z cr						$\pi_{16} > 0$, $d_{11} > 0$	
$6/m$	∥ 6	⊥ Z cr						$\pi_{16} > 0$	
622	∥ 6	⊥ Z cr							$d_{14} > 0$
$6mmm$	∥ 6	⊥ Z cr						$d_{33} > 0$	
$\bar{6}m^2$	∥ $\bar{6}$	⊥ m						$d_{22} > 0$	
$6/mmm$	∥ 6	⊥ Z cr							

Table A.2 (cont'd)

Class	Z [001]	X [100]	Y [010]	α, β, γ	X_3	X_1	X_2	Choice of coordinate system	Right-hand modification
				Cubic system					
23	$\parallel 2$			$\alpha=\beta=\gamma=90°$	[001[	[100]	[010]	$\pi_{12}>\pi_{21}$	$d_{14}>0$
$m3$	$\parallel 2$							$\pi_{12}>\pi_{21}$	
432	$\parallel 4$								$G>0$
$43m$	$\parallel \bar{4}$							$d_{14}>0$	
$m3m$	$\parallel 4$								
				Possible changes					
2	$\parallel 2$	$\perp Z\,cr_1$	$\perp Z\,cr_2$	$\alpha=\beta=90°$ $\gamma>90°$	[001]	[100]	$\perp$ (010)		$d_{33}>0$
m	$\perp m$	$\perp Z\,cr_1$	$\perp Z\,cr_2$					$d_{11}>0$	
$2/m$	$\parallel 2$	$\perp Y\,cr_1$	$\perp Z\,cr_2$	$\alpha=\beta=90°$, $\gamma=120°$	[0001]	$[2\bar{1}\bar{1}0]$	$[01\bar{1}0]$		
$\bar{6}2m$	$\parallel \bar{6}$	$\parallel 2$						$d_{11}>0$	

indices are related to the primitive lattice and to rows, the unprimed indices are related to centred lattices and to columns).

Some Relations Between the Parameters of the Primitive Bravais Lattices Facilitating the Use of Table B.1 Are as Follows:

Primitive triclinic lattice $P\bar{1}$:

$$\omega = \sqrt{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma},$$

$$a^* = \frac{\sin\alpha}{a\omega}, \quad b^* = \frac{\sin\beta}{b\omega}, \quad c^* = \frac{\sin\gamma}{c\omega},$$

$$\cos\alpha^* = \frac{\cos\beta\cos\gamma-\cos\alpha}{\sin\beta\sin\gamma}, \quad \cos\beta^* = \frac{\cos\gamma\cos\alpha-\cos\beta}{\sin\gamma\sin\alpha},$$

$$\cos\gamma^* = \frac{\cos\alpha\cos\beta-\cos\gamma}{\sin\alpha\sin\beta}.$$

Primitive monoclinic lattice $P2/m$:

$$\alpha=\gamma=90°, \quad \omega=\sin\beta,$$

$$a^* = 1/a\sin\beta, \quad b^* = 1/b, \quad c^* = 1/c\sin\beta, \quad \alpha^*=\gamma^*=90°, \quad \beta^*=180°-\beta.$$

Primitive rhombic lattice $Pmmm$:

$$\alpha=\beta=\gamma=90°, \quad \omega=1,$$

$$a^*=1/a, \quad b^*=1/b, \quad c^*=1/c, \quad \alpha^*=\beta^*=\gamma^*=90°.$$

Primitive tetragonal lattice $P4/mmm$:

$$a=b, \quad \alpha=\beta=\gamma=90°, \quad \omega=1, \quad a^*=b^*=1/a, \quad \alpha^*=\beta^*=\gamma^*=90°.$$

Primitive hexagonal lattice $P6/mmm$:

$$a=b, \quad \alpha=\beta=90°, \quad \gamma=120°, \quad \omega=\sqrt{3/2},$$

$$a^*=b^*=2(a\sqrt{3})^{-1}, \quad c^*=1/c, \quad \alpha^*=\beta^*=90°, \quad \gamma^*=60°.$$

Primitive cubic lattice:

$$a=b=c, \quad \alpha=\beta=\gamma=90°, \quad \omega=1,$$

$$a^*=b^*=c^*=1/a, \quad \alpha^*=\beta^*=\gamma^*=90°.$$

C. PROPERTIES OF DIRECTIONS IN CRYSTALS

By the character of their array with respect to the symmetry elements of a crystal the directions in it are divided into singular and non-singular, polar and non-polar, axial and non-axial, screw and non-screw* ones. Here we have used the traditional term "direction", but it would be more correct to speak of straight lines in the present context.

A straight line is called *singular* if all the symmetry operations of the point group of a crystal transform this line only into itself.

Let us connect a polar vector with a given straight line. If at least one of the symmetry operations of the crystal's point group transforms this straight line into itself and the vector into its opposite, the straight line is called *non-polar*.

Let us connect an axial vector with a straight line. If at least one of the symmetry operations of the crystal's point group transforms the straight line into itself and the axial vector into its opposite, the straight line is called *non-axial*.

* See also Zheludev (1971).

Table B.1

Matrices A, E, G and G^{-1} for Primitive Bravais Lattices

Lattice	A	E	G	G^{-1}
Triclinic $P\bar{1}$	$\begin{matrix} a\sin\beta & 0 & a\cos\beta \\ -b\sin\alpha\cos\gamma^* & \frac{b\omega}{\sin\beta} & b\cos\alpha \\ 0 & 0 & c \end{matrix}$	$\begin{matrix} \frac{a^*\omega}{\sin\alpha\sin\beta} & 0 & -\frac{c^*\omega}{\tan\beta\sin\gamma} \\ a^*\cos\gamma^* & b^* & c^*\cos\alpha^* \\ 0 & 0 & \frac{c^*\omega}{\sin\gamma} \end{matrix}$	$\begin{matrix} a^2 & ab\cos\gamma & ca\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ca\cos\beta & bc\cos\alpha & c^2 \end{matrix}$	$\begin{matrix} a^{*2} & a^*b^*\cos\gamma^* & c^*a^*\cos b^* \\ a^*b^*\cos\gamma^* & b^{*2} & b^*c^*\cos\alpha^* \\ c^*a^*\cos\beta^* & b^*c^*\cos\alpha^* & c^{*2} \end{matrix}$
Monoclinic $P2/m$	$\begin{matrix} a\sin\beta & 0 & a\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c \end{matrix}$	$\begin{matrix} a^* & 0 & -c^*\cos\beta \\ 0 & b^* & 0 \\ 0 & 0 & c^*\sin\beta \end{matrix}$	$\begin{matrix} a^2 & 0 & ca\cos\beta \\ 0 & b^2 & 0 \\ ca\cos b & 0 & c^2 \end{matrix}$	$\begin{matrix} a^{*2} & 0 & c^*a^*\cos\beta^* \\ 0 & b^{*2} & 0 \\ c^*a^*\cos\beta^* & 0 & c^{*2} \end{matrix}$
Rhombic $Pmmm$	$\begin{matrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{matrix}$	$\begin{matrix} a^* & 0 & 0 \\ 0 & b^* & 0 \\ 0 & 0 & c^* \end{matrix}$	$\begin{matrix} a^2 & 0 & 0 \\ 0 & b^2 & 0 \\ 0 & 0 & c^2 \end{matrix}$	$\begin{matrix} a^{*2} & 0 & 0 \\ 0 & b^{*2} & 0 \\ 0 & 0 & c^{*2} \end{matrix}$
Tetragonal $P4/mmm$	$\begin{matrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{matrix}$	$\begin{matrix} a^* & 0 & 0 \\ 0 & a^* & 0 \\ 0 & 0 & c^* \end{matrix}$	$\begin{matrix} a^2 & 0 & 0 \\ 0 & a^2 & 0 \\ 0 & 0 & c^2 \end{matrix}$	$\begin{matrix} a^{*2} & 0 & 0 \\ 0 & a^{*2} & 0 \\ 0 & 0 & c^{*2} \end{matrix}$
Hexagonal $P6/mmm$	$\begin{matrix} a & 0 & 0 \\ -\frac{a}{2} & \frac{a\sqrt{3}}{2} & 0 \\ 0 & 0 & c \end{matrix}$	$\begin{matrix} \frac{a^*\sqrt{3}}{2} & 0 & 0 \\ \frac{a^*}{2} & a^* & 0 \\ 0 & 0 & c^* \end{matrix}$	$\begin{matrix} a^2 & -\frac{a^2}{2} & 0 \\ -\frac{a^2}{2} & a^2 & 0 \\ 0 & 0 & c^2 \end{matrix}$	$\begin{matrix} a^{*2} & \frac{a^{*2}}{2} & 0 \\ \frac{a^{2*}}{2} & a^{*2} & 0 \\ 0 & 0 & c^{*2} \end{matrix}$
Cubic $Pm3m$	$\begin{matrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{matrix}$	$\begin{matrix} a^* & 0 & 0 \\ 0 & a^* & 0 \\ 0 & 0 & a^* \end{matrix}$	$\begin{matrix} a^2 & 0 & 0 \\ 0 & a^2 & 0 \\ 0 & 0 & a^2 \end{matrix}$	$\begin{matrix} a^{*2} & 0 & 0 \\ 0 & a^{*2} & 0 \\ 0 & 0 & a^{*2} \end{matrix}$

Table B.2

Matrices G and G^{-1} for Centred Bravais Lattices

Lattice	G			G^{-1}		
$C2/m$	a^2	$a^2\cos\gamma$	$ac\cos\alpha$	a^{*2}	$a^{*2}\cos\gamma^*$	$a^*c^*\cos\alpha^*$
	$a^2\cos\gamma$	a^2	$ac\cos\alpha$	$a^{*2}\cos\gamma^*$	a^{*2}	$a^*c^*\cos\alpha^*$
	$ac\cos\alpha$	$ac\cos\alpha$	c^2	$a^*c^*\cos\alpha^*$	$a^*c^*\cos\alpha^*$	c^{*2}
$Cmmm$	a^2	$a^2\cos\gamma$	0	a^{*2}	$a^{*2}\cos\gamma^*$	0
	$a^2\cos\gamma$	a^2	0	$a^{*2}\cos\gamma^*$	a^{*2}	0
	0	0	c^2	0	0	c^{*2}
$Fmmm$	a^2	$\frac{a^2+b^2-c^2}{2}$	$\frac{a^2-b^2+c^2}{2}$	a^{*2}	$a^{*2}\cos\gamma^*$	$a^{*2}\cos\beta^*$
	$\frac{a^2+b^2-c^2}{2}$	b^2	$\frac{-a^2+b^2+c^2}{2}$	$a^{*2}\cos\gamma^*$	a^{*2}	$a^{*2}\cos\alpha^*$
	$\frac{a^2-b^2+c^2}{2}$	$\frac{-a^2+b^2+c^2}{2}$	c^2	$a^{*2}\cos\beta^*$	$a^{*2}\cos\alpha^*$	a^{*2}
$Immm$	a^2	$a^2\cos\gamma$	$a^2\cos\beta$	a^{*2}	$\frac{a^{*2}+b^{2*}-c^{2*}}{2}$	$\frac{a^{*2}-b^{*2}+c^{*2}}{2}$
	$a^2\cos\gamma$	a^2	$a^2\cos\alpha$	$\frac{a^{*2}+b^{*2}-c^{*2}}{2}$	b^{*2}	$\frac{-a^{*2}+b^{*2}+c^{*2}}{2}$
	$a^2\cos\beta$	$a^2\cos\alpha$	a^2	$\frac{a^{*2}-b^{*2}+c^{*2}}{2}$	$\frac{-a^{*2}+b^{*2}+c^{*2}}{2}$	c^{*2}

$I4/mmm$	a^2	$-a^2(1+2\cos\alpha)$	$a^2\cos\alpha$	a^{*2}	$\frac{2a^{*2}-c^{*2}}{2}$	$\frac{c^{*2}}{2}$
	$-a^2(1+2\cos\alpha)$	a^2	$a^2\cos\alpha$	$\frac{2a^{*2}-c^{*2}}{2}$	a^{*2}	$\frac{c^{*2}}{2}$
	$a^2\cos\alpha$	$a^2\cos\alpha$	a^2	$\frac{c^{*2}}{2}$	$\frac{c^{*2}}{2}$	c^{*2}
$R\bar{3}m$	a^2	$a^2\cos\alpha$	$a^2\cos\alpha$	a^{*2}	$a^{*2}\cos\alpha^*$	$a^{*2}\cos\alpha^*$
	$a^2\cos\alpha$	a^2	$a^2\cos\alpha$	$a^{*2}\cos\alpha^*$	a^{*2}	$a^{*2}\cos\alpha^*$
	$a^2\cos\alpha$	$a^2\cos\alpha$	a^2	$a^{*2}\cos\alpha^*$	$a^{*2}\cos\alpha^*$	a^{*2}
$Fm3m$	a^2	$\frac{a^2}{2}$	$\frac{a^2}{2}$	a^{*2}	$-\frac{a^{*2}}{3}$	$-\frac{a^{*2}}{3}$
	$\frac{a^2}{2}$	a^2	$\frac{a^2}{2}$	$-\frac{a^{*2}}{3}$	a^{*2}	$-\frac{a^{*2}}{3}$
	$\frac{a^2}{2}$	$\frac{a^2}{2}$	a^2	$-\frac{a^{*2}}{3}$	$-\frac{a^{*2}}{3}$	a^{*2}
$Im3m$	a^2	$-\frac{a^2}{3}$	$-\frac{a^2}{3}$	a^{*2}	$\frac{a^{*2}}{2}$	$\frac{a^{*2}}{2}$
	$-\frac{a^2}{3}$	a^2	$-\frac{a^2}{3}$	$\frac{a^{*2}}{2}$	a^{*2}	$\frac{a^{*2}}{2}$
	$-\frac{a^2}{3}$	$-\frac{a^2}{3}$	a^2	$\frac{a^{*2}}{2}$	$\frac{a^{*2}}{2}$	a^{*2}

Table B.3

Matrices Q and P Connecting Vector Bases of Centred Bravais Lattices with the Bases of the Corresponding Primitive Lattices

Lattices	$C2/m$ $Cmmm$	$Fmmm$ $Fm3m$	$Immm$ $I4/mmm$ $Im3m$	$R\bar{3}m$
Q	$\begin{matrix} 1/2 & -1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{matrix}$	$\begin{matrix} 0 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \\ 1/2 & 1/2 & 0 \end{matrix}$	$\begin{matrix} -1/2 & 1/2 & 1/2 \\ 1/2 & -1/2 & 1/2 \\ 1/2 & 1/2 & -1/2 \end{matrix}$	$\begin{matrix} 2/3 & 1/3 & 1/3 \\ -1/3 & 1/3 & 1/3 \\ -1/3 & -2/3 & 1/3 \end{matrix}$
P	$\begin{matrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}$	$\begin{matrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{matrix}$	$\begin{matrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{matrix}$	$\begin{matrix} 1 & -1 & 0 \\ 0 & 1 & -1 \\ 1 & 1 & 1 \end{matrix}$

Let us, finally, connect a screw with a straight line. If at least one of the symmetry operations of the crystal's point group transforms this straight line into itself and the screw into one of the opposite sense, the straight line is called a *non-screw* one.

The corresponding definitions can be introduced in another way—with the aid of the Curie limit groups. The symmetry group of an isolated straight line, $G_l = \infty/mm$, with axis ∞ coinciding with the straight line; the symmetry group of a straight line in a crystal, $G_{l.cr}$, we shall call it the simple symmetry group of the straight line, is the intersection of the point group of the crystal, G_{cr}, with the group G_l

$$G_{l.\,cr} = G_{cr} \cap G_l$$

A straight line is called *singular*, if its symmetry group coincides with the symmetry group of the crystal:

$$G_{l.cr} = G_{cr}$$

apparently, in the corresponding case it is necessary and sufficient for the symmetry group of the crystal to be a subgroup of the group of the isolated straight line (certainly with account taken of the mutual array of crystal and line):

$$G_{cr} \subset G_l = \infty/mm.$$

Hence it directly follows that singular straight lines are available in those and only in those crystals, whose point groups are the subgroups of the limit group ∞/mm; such are the crystals of the lower and intermediate categories.

A straight line is called *polar*, if its symmetry group is a subgroup of the polar vector group: $G_{l.cr} \subset \infty m$. It is called *axial* if its symmetry group is a subgroup of the axial vector group: $G_{l.cr} \subset \infty/m$. Finally, it is called a *screw* straight line if its symmetry group is a subgroup of the screw group: $G_{l.cr} \subset \infty 2$.

The listed characteristics of directions (we return to the traditional terminology) are important for crystal physics. Thus, an isolated* eigenvector of a symmetric second-rank matter tensor always coincides with one of the singular directions of a crystal. Only crystals with at least one singular polar direction

* That is, contained neither in the plane, nor in the space of eigenvectors.

Table C.1

Directions in Crystals

Class	Non-polar	Non-axial	Non-screw	Singular			
				polar	axial	screw	others
1	—	—	—	*hkl*	*hkl*	*hkl*	—
$\bar{1}$	*hkl*	—	*hkl*	—	*hkl*	—	—
2	*h*0*l*	*h*0*l*	—	010	010	010 *h*0*l*	—
m	010	*h*0*l*	010 *h*0*l*	*h*0*l*	010	—	—
2/*m*	*hkl*	*h*0*l*	*hkl*	—	010	—	*h*0*l*
222	0*kl* *h*0*l* *hk*0	0*kl* *h*0*l* *hk*0	—	—	—	100 010 001	—
*mm*2	*hk*0	0*kl* *h*0*l* *hk*0	0*kl* *h*0*l*	001	—	—	100 010
mmm	*hkl*	0*kl* *h*0*l* *hk*0	*hkl*	—	—	—	100 010 001
3	—	—	—	0001	0001	0001	—
$\bar{3}$	*hkil*	—	*hkil*	—	0001	—	—
32	$0k\bar{k}i$	$0k\bar{k}l$	—	—	—	0001	—
3*m*	$2\bar{1}\bar{1}0$	$0k\bar{k}l$	$2\bar{1}\bar{1}0$ $0k\bar{k}l$	0001	—	—	—
$\bar{3}m$	*hkil*	$0k\bar{k}l$	*hkil*	—	—	—	0001
4	*hk*0	*hk*0	—	001	001	001	—
$\bar{4}$	*hk*0 001	*hk*0	001	—	001	—	—
4/*m*	*hkl*	*hk*0	*hkl*	—	001	—	—
422	*hk*0 0*kl* *hhl*	*hk*0 0*kl* *hhl*	—	—	—	001	—

Table C.1 (cont'd)

Class	Non-polar	Non-axial	Non-screw	Singular			
				polar	axial	screw	others
$4mm$	$hk0$	$hk0$ $0kl$ hhl	$0kl$ hhl	001	—	—	
$\bar{4}2m$	$hk0$ $0kl$	$hk0$ $0kl$ hhl	hhl	—	—	—	001
$4/mmm$	hkl	$hk0$ $0kl$ hhl	hkl	—	—	—	001
6	$hki0$	$hki0$	—	0001	0001	0001	—
$\bar{6}$	$hki0$ 0001	$hki0$	$hki0$ 0001	—	0001	—	—
$6/m$	$hkil$	$hki0$	$hkil$	—	0001	—	—
622	$hki0$ $0k\bar{k}l$ $hkkl$	$hki0$ $0k\bar{k}l$ $hkkl$	—	—	—	0001	—
$6mm$	$hki0$	$hki0$ $0k\bar{k}l$ $hkkl$	$0k\bar{k}l$ $hkkl$	0001	—	—	—
$\bar{6}m2$	$hki0$ $hkkl$	$hki0$ $0k\bar{k}l$ $hkkl$	$hki0$ $0k\bar{k}l$	—	—	—	0001
$6/mmm$	$hkil$	$hki0$ $0k\bar{k}l$ $hkkl$	$hkil$	—	—	—	0001
23	$0kl$	$0kl$	—	—	—	—	—
$m3$	hkl	$0kl$	hkl				
432	$0kl$ hhl	$0kl$ hhl	—	—	—	—	—
$\bar{4}3m$	$0kl$	$0kl$ hhl	hhl				

Table C.1 (cont'd)

Class	Non-polar	Non-axial	Non-screw	Singular			
				polar	axial	screw	others
$m3m$	hkl	$0kl$ hhl	hkl	—	—	—	—

can be pyroelectrics; only such a direction can be the direction of the vectors of spontaneous polarization, spontaneous electric induction, and pyroelectric coefficients. Only a polar direction can be the direction of piezoelectric polarization. Finally, circular or elliptic birefringence of the screw type is possible only in the screw direction (the possibility of axial-type birefringence is determined by the magnetic symmetry of the direction, see Sec. 82).

The polar, axial and screw directions are shown in Fig. 44.1. The characteristics of all possible bundles of symmetrically equivalent directions for all the 32 classes of crystal symmetry are given in Table C.1. The bundles of symmetrically equivalent directions in crystals of the hexagonal system (trigonal and hexagonal systems) are characterized by the Bravais indices, in the crystals of all other classes, by the Miller indices. The orientation is standard (see Appendix A). Table C.2 shows the properties of directions in the media of limit

Table C.2

Directions in Media of Limit Symmetry

Curie group	Non-polar	Non-axial	Non-screw	Singular			
				polar	axial	screw	others
∞	$\perp k$	$\perp k$	none	k	k	k	none
∞/m	all	$\perp k$	all	none	k	none	none
$\infty 2$	all	all	none	none	none	k	none
∞m	$\perp k$	all	all	k	none	none	none
∞/mm	all	all	all	none	none	none	k
$\infty\infty$	all	all	none	none	none	none	none
$\infty\infty m$	all	all	all	none	none	none	none

Note. Vector k is directed along the principal symmetry axis.

symmetry. It can be seen from the Table that properties related to an axial vector are the same in all crystals of the same subsystem. The reason for this is that an axial vector is invariant with respect to inversion.

D. ANALYTICAL PROOF OF THEOREMS ON THE MULTIPLICATION OF SYMMETRY OPERATIONS

Theorems on the multiplication of symmetry operations given in Sec. 3, are easily proved analytically by multiplying the corresponding matrices; the method of composing these matrices is given in Sec. 17, and the matrices themselves are given in Table 17.1.

List of Tables in Appendix E

Table No.	Internal symmetry	Usage
E. 1	ε	Enantiomorphism ρ: for the right-handed crystals $\rho = 1$, for the left-handed ones $\rho = -1$, for non-enantiomorphous ones $\rho = 0$ (Sec. 5): specific rotation of the polarization plane α in optically isotropic substances (Sec. 81).
E. 2	V	Vectors of pyroelectric coefficients p (Sec. 31), of spontaneous polarization $P^{(0)}$ and spontaneous induction $D^{(0)}$ (Secs. 26, 65), of piezoelectric polarization under hydrostatic pressure $d = \mathbf{d} : \mathbf{I}$ (Sec. 58).
E. 3	εV	Axial vectors; they are dual of tensors $\{V^2\}$ (see Table E. 5). Apparently not used as independent matter tensors. It had been supposed that such was the vector of pyromagnetic coefficients, but upon the discovery of the magnetic symmetry of crystals this conception was proved to be erroneous.
E. 4	$[V^2]$	Tensors of spontaneous strain $\varepsilon^{(0)}$ (Sec. 65), of dielectric susceptibility α, permittivity $\varkappa$ and impermeability η (Secs. 26, 27), magnetic permittivity μ (Sec. 73), thermal expansion α and thermoelasticity β (Secs. 51, 52) and many others, as well as tensors of electrical conductivity σ, specific electrical resistance ρ, thermal conductivity λ and temperature diffusivity $\mathbf{k}$ for non-magnetic crystals (Secs. 32, 33, 76).
E. 5	$\{V^2\}$	Antisymmetric parts of tensors of type V^2 (Table E. 6) apparently are not used in practice as independent matter tensors.
E. 6	V^2	Tensors of Faraday's coefficients $\mathbf{F}$ (Sec. 82), of thermoelectric coefficients α and γ (Sec. 76), tensors $\mathbf{R}$ of Hall's coefficients and $\mathbf{L}$ of Righi-Leduc coefficients in non-magnetic crystals (Sec. 76), and tensors of electrical conductivity σ, electrical resistance ρ and thermal conductivity λ in magnetic crystals (Sec. 76).
E. 7	$\varepsilon [V^2]$	Symmetric pseudotensor of gyration coefficients $\mathbf{G}$ (Secs. 81, 82).
E. 8	$\varepsilon \{V^2\}$	Antisymmetric part of a complete pseudotensor of gyration; it describes only "weak" optical activity (Sec. 81).
E. 9	εV^2	Full (non-symmetric) pseudotensor of gyration coefficients; it describes, along with the ordinary ("strong") optical activity, also the "weak" one (Sec. 81).
E. 10	$[V^3]$	Tensor of the longitudinal piezoelectric effect $\mathbf{f}$ (Sec. 58); tensor of the quadratic dielectric susceptibility $\chi(2\omega, \omega, \omega)$, dispersion being neglected (Secs. 79, 80).

(*cont'd*)

Table No.	Internal symmetry	Usage
E. 11	$V[V^2]$	Tensors of piezoelectric coefficients **d** and **e** (Secs. 58, 60, 61), of electrooptical effect **r** (Sec. 77), of quadratic susceptibility coefficients χ (2ω, ω, ω) and χ (0, ω, ω) (Sec. 79).
E. 12	$\{V^2\}V$	Matter tensor γ characterizing spatial dispersion of the first order (Sec. 81).
E. 13	V^3	Tensor of quadratic susceptibility $\chi(\omega_1 \pm \omega_2, \omega_1, \omega_2)$ when $\omega_1 \neq \omega_2$ and dispersion is taken into consideration (Sec. 79).
E. 14	$\varepsilon V[V^2]$	Pseudotensor of electrogyration **A** characterizing the change of a symmetric pseudotensor of gyration under the influence of electric field (Sec. 82). Earlier it was erroneously believed that such were also the piezomagnetic coefficients (cf. crystal-physical usage of an axial vector, E. 3).
E. 15	εV^3	Pseudotensors of Nernst and Ettingshausen coefficients **N** and **M** (Sec. 76); pseudotensors of Hall's coefficients **P** and Righi-Leduc coefficients **Q** in magnetic crystals (Sec. 76).
E. 16	$[V^4]$	Tensor of cubic susceptibility θ (3ω, ω, ω, ω) with dispersion being neglected (Sec. 79).
E. 17	$V[V^3]$	Tensor of cubic susceptibility θ (3ω, ω, ω, ω) (Sec. 79).
E. 18	$[[V^2]^2]$	Tensors of elasticity coefficients **c** and elastic compliance **s** (Secs. 51, 52).
E. 19	$[V^2]^2$	Tensors of electrostriction coefficients **P** (Sec. 74), of magnetostriction, elastoresistive **m** and piezoresistive **Π** coefficients (Sec. 75), elastooptical **p**, piezooptical coefficients π (Sec. 77), Kerr's coefficients **K** (Secs. 77, 79) and Cotton-Mouton coefficients **C** (Sec. 82).
E. 20	$[(V^2)^2]$	Tensors of elastic coefficients in symmetric theories of elasticity.
E. 21	$[V^2]V^2$	Tensor of cubic susceptibility θ (2ω, 0, ω, ω) describes the generation of a second harmonic of electromagnetic radiation in centrosymmetric crystals placed in an electric field (Secs. 79, 80).
E. 22	V^4	General tensor of cubic susceptibility $\theta(\omega, \omega_1, \omega_2, \omega_3)$ (Sec. 79).
E. 23	$V[[V^2]^2]$	Tensor of quadratic piezoelectric effect **Q**, tensor of the effect of electric field on elastic constants, etc. (Sec. 74).
E. 24	$[[V^2]^3]$	Quadratic coefficients of elasticity **C** and of elastic compliance **L** (Sec. 74).
E. 25	$[V^2][[V^2]^2]$	Coefficients of the effect of static stress or strain on dynamic elastic constants (Sec. 74), of the quadratic piezooptical effect, etc.

Theorem 1. By multiplying out the matrices of rotation about axis 2 and of reflection in a plane perpendicular to it (2_z and m_z)

$$\begin{Vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{Vmatrix} \begin{Vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{Vmatrix} = \begin{Vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{Vmatrix},$$

we obtain an inversion matrix. Other theorems are proved similarly.

Theorem 2. It can be considered, without loss of generality, that one of the planes intersecting each other at an angle ψ is perpendicular to the base vector e_1, while the unit vector of the perpendicular to the second plane is $e_1 \cos\psi + e_2 \sin\psi$. Let us take from the Table and multiply out the corresponding matrices:

$$\begin{Vmatrix} -\cos 2\psi & -\sin 2\psi & 0 \\ -\sin 2\psi & \cos 2\psi & 0 \\ 0 & 0 & 1 \end{Vmatrix} \begin{Vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{Vmatrix} = \begin{Vmatrix} \cos 2\psi & -\sin 2\psi & 0 \\ \sin 2\psi & \cos 2\psi & 0 \\ 0 & 0 & 1 \end{Vmatrix}.$$

As a result we have the matrix of rotation about the vector e_3 (i.e. about the line of the intersection of the planes) through angle 2ψ.

E. TENSORS INVARIANT WITH RESPECT TO CRYSTALLOGRAPHIC AND LIMIT GROUPS

The tables in this Appendix list the tensors and pseudotensors of different internal symmetry invariant with respect to all possible crystallographic and limit groups; to save space, in the last three tables the fifth- and sixth-rank tensors are given only for a few classes*. The internal symmetry of tensors is denoted in the headings of the tables by Jahn symbols, which are described in detail in Sec. 42. The numbers of independent components and invariants are given for all tensors (the number of the components being given alone means that the number of independent invariants is the same). Tensors (and pseudotensors) invariant with respect to the specified crystallographic and limit groups are used in crystal-physics as matter tensors of the crystals and textures related to the corresponding crystallographic and limit groups. The crystal-physical uses of the tensors listed in this Appendix are given in the following pages.

* Fuller tables, to the eighth rank inclusive, were composed by Smith (1970).

Table E.1

ε-Pseudoscalar ρ

Classes	ρ
1, 2, 222, 3, 32, 4, 422, 6, 622, 23, 432, ∞, ∞2, ∞∞	ρ
$\bar{1}$, m, $2/m$, $mm2$, mmm, $\bar{3}$, $3m$, $\bar{3}m$, 4, $4/m$, $4mm$, $\bar{4}2m$, $4/mmm$, $\bar{6}$, $6/m$, $6mm$, $\bar{6}m2$, $6/mmm$, $m3$, $\bar{4}3m$, $m3m$, ∞/m, ∞m, ∞/mm, $\infty\infty m$	0

Table E.2

V—Vector p

Classes	p_i	Classes	p_i
1 — 3 comp., 1 inv. *)	p_1 p_2 p_3	2 ($2 \parallel X_2$) — 1 comp.,	0 p_2 0
m ($m \perp X_2$) — 2 comp, 1 inv.	p_1 0 p_3	2 ($2 \parallel X_3$), $mm2$, 3, $3m$, 4, $4mm$,	0 0 p_3
m ($m \perp X_3$) — 2 comp., 1 inv.	p_1 p_2 0	6, $6mm$, ∞, ∞m — 1 comp.	

In classes $\bar{1}$, $2/m$, 222, mmm, $\bar{3}$, 32, $\bar{3}m$, $\bar{4}$, $4/m$, 422, $\bar{4}2m$, $4/mmm$, $\bar{6}$, $6/m$, 622, $\bar{6}m2$, $6/mmm$, 23, $m3$, 432, $\bar{4}3m$, $m3m$, ∞/m, $\infty 2$, ∞/mm, $\infty\infty$, $\infty\infty m$ $p = 0$.

*"3 comp., 1 inv." means that the matter tensor in this class has 3 independent components and 1 independent invariant. These abbreviations are used in all tables of this Appendix. When only the number of independent components is given, it means that the number of independent invariants is the same.

Table E.3

εV—Axial Vector $\mathring{a}$

Classes	a_i
1, $\bar{1}$ — 3 comp. 1 inv.	a_1 a_2 a_3
2, m, $2/m$ ($2 \parallel X_2$, $m \perp X_2$) — 1 comp.	0 a_2 0
2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$), 3, $\bar{3}$, 4, 4, $4/m$, 6, $\bar{6}$, $6/m$, ∞, ∞/m — 1 comp.	0 0 a_3

In classes 222, $mm2$, mmm, 32, $3m$, $\bar{3}m$, 422, $4mm$, $\bar{4}2m$, $4/mmm$, 622, $6mm$, $\bar{6}m2$, $6/mmm$, 23, $m3$, 432, $\bar{4}3m$, $m3m$, $\infty 2$, ∞m, ∞/mm, $\infty\infty$, $\infty\infty m$ $\mathring{a} \equiv 0$.

Table E.4

$[V^2]$—Symmetric Second-Rank Tensor S; $S_{ij}=S_{ji}$

Classes	S_{ij}	Classes	S_{ij}
1, $\bar{1}$ 6 comp., 3 inv.	S_{11} S_{12} S_{31} S_{22} S_{23} S_{33}	222, $mm2$, mmm 3 comp..	S_{11} 0 0 S_{22} 0 S_{33}
2, m, $2/m$ ($2 \parallel X_2$, $m \perp X_2$) 4 comp., 3 inv.	S_{11} 0 S_{31} S_{22} 0 S_{33}	3, $\bar{3}$, 32, $3m$, $\bar{3}m$, 4, $\bar{4}$, $4/m$, 422, $4mm$, $\bar{4}2m$, $4/mmm$, 6, $\bar{6}$, $6/m$, 622, $6mm$, $\bar{6}m2$, $6/mmm$, ∞, ∞/m, $\infty 2$, ∞m, ∞/mm — 2 comp..	S_{11} 0 0 S_{11} 0 S_{33}
2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$) 4 comp., 3 inv.	S_{11} S_{12} 0 S_{22} 0 S_{33}	23, $m3$, 432, $\bar{4}3m$, $m3m$, $\infty\infty$, $\infty\infty m$, 1 comp.	S_{11} 0 0 S_{11} 0 S_{11}

Table E.5

$\{V^2\}$—Antisymmetric Second-Rank Tensor A; $A_{ji}=-A_{ij}$

Classes	A_{ij}	Classes	A_{ij}
1, $\bar{1}$ 3 comp., 1 inv.	0 A_{12} $-A_{31}$ $-A_{12}$ 0 A_{23} A_{31} $-A_{23}$ 0	2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$), 3, $\bar{3}$, 4, $\bar{4}$, $4/m$, 6, $\bar{6}$, $6/m$ ∞, ∞/m 1 comp.	0 A_{12} 0 $-A_{12}$ 0 0 0 0 0
2, m, $2/m$ ($2 \parallel X_2$, $m \perp X_2$) 1 comp.	0 0 $-A_{31}$ 0 0 0 A_{31} 0 0		

In classes 222, $mm2$, mmm, 32, $3m$, $\bar{3}m$, 422, $4mm$, $\bar{4}2m$, $4/mmm$, 622, $6mm$, $\bar{6}m2$, $6/mmm$, 23, $m3$, 432, $\bar{4}3m$, $m3m$, $\infty 2$, ∞m, ∞/mm, $\infty\infty$, $\infty\infty m$ $A=0$.

Table E.6

V^2—Second-Rank Tensor T

Classes	T_{ij}	Classes	T_{ij}
1, $\bar{1}$ 9 comp., 6 inv.	T_{11} T_{12} T_{13} T_{21} T_{22} T_{23} T_{31} T_{32} T_{33}	2, m, $2/m$ ($2 \parallel X_2$, $m \perp X_2$) 5 comp., 4 inv.	T_{11} 0 T_{13} 0 T_{22} 0 T_{31} 0 T_{33}

Table E.6. (cont'd)

Classes	T_{ij}	Classes	T_{ij}
2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$) 5 comp. 4 inv.	T_{11} T_{12} 0 T_{21} T_{22} 0 0 0 T_{33}	32, $3m$, $\bar{3}m$, 422, $4mm$, $42m$, $4/mmm$, 622, $6mm$, $\bar{6}m2$, $6/mmm$, $\infty 2$, ∞m, ∞/mm — 2 comp.	T_{11} 0 0 0 T_{11} 0 0 0 T_{33}
222, $mm2$, mmm 3 comp.	T_{11} 0 0 0 T_{22} 0 0 0 T_{33}	23, $m3$, 432, $\bar{4}3m$ $m3m$, $\infty\infty$, $\infty\infty m$ 1 comp.	T_{11} 0 0 0 T_{11} 0 0 0 T_{11}
3, $\bar{3}$, 4, $\bar{4}$, $4/m$, 6, $\bar{6}$, $6/m$, ∞, ∞/m 3 comp.	T_{11} T_{12} 0 $-T_{12}$ T_{11} 0 0 0 T_{33}		

Table E.7

ε [V^2]—Symmetric Second-Rank Tensor G; $G_{ji}=G_{ij}$

Class	G_{ij}	Class	G_{ij}	Class	G_{ij}
1 6 comp., 3 inv.	G_{11} G_{12} G_{31} G_{22} G_{23} G_{33}	m ($m \perp X_3$) 2 comp., 1 inv.	0 0 G_{31} 0 G_{23} 0	$\bar{4}2\,m$ 1 comp.	G_{11} 0 0 $-G_{11}$ 0 0
2 ($2 \parallel X_3$) 4 comp., 3 inv.	G_{11} 0 G_{31} G_{22} 0 G_{33}	222 3 comp.	G_{11} 0 0 G_{22} 0 G_{33}	3, 32, 4 422, 6, 622, ∞, $\infty 2$ 2 comp.	G_{11} 0 0 G_{11} 0 G_{33}
2 ($2 \parallel X_3$) 4 comp., 3 inv.	G_{11} G_{12} 0 G_{22} 0 G_{33}	$mm2$, $\bar{4}m2$ ($m \perp X_1$, X_2) 1 comp.	0 G_{12} 0 0 0 0	23, 432, $\infty\infty$ 1 comp.	G_{11} 0 0 G_{11} 0 G_{11}
m ($m \perp X_2$) 2 comp., 1 inv.	0 G_{12} 0 0 G_{23} 0	$\bar{4}$ 2 comp., 1 inv.	G_{11} G_{12} 0 $-G_{11}$ 0 0		

In classes $\bar{1}$, $2/m$, mmm, $\bar{3}$, $3m$, $\bar{3}m$, $4/m$, $4mm$, $\bar{6}$, $6/m$, $6mm$, $\bar{6}m2$, $6/mmm$, $m3$, $\bar{4}3m$, $m3m$, ∞/m, ∞m, ∞/mm, $\infty\infty m$ **G** = 0.

Table E.8

$\varepsilon\{V^2\}$—Antisymmetric Second-Rank Pseudotensor B; $B_{ji} = -B_{ij}$

Classes	B_{ij}	Classes	B_{ij}
1 3 comp., 1 inv.	$\begin{matrix} 0 & B_{12} & -B_{31} \\ -B_{12} & 0 & B_{23} \\ B_{31} & -B_{23} & 0 \end{matrix}$	$m\ (m \perp X_3)$ 2 comp., 1 inv.	$\begin{matrix} 0 & 0 & -B_{31} \\ 0 & 0 & B_{23} \\ B_{31} & -B_{23} & 0 \end{matrix}$
$2\ (2 \parallel X_2)$ 1 comp.,	$\begin{matrix} 0 & 0 & -B_{31} \\ 0 & 0 & 0 \\ B_{31} & 0 & 0 \end{matrix}$	$2\ (2 \parallel X_3)$, $mm2$, 3, $3m$ 4, $4mm$, 6, $6mm$, ∞, ∞m 1 comp.	$\begin{matrix} 0 & B_{12} & 0 \\ -B_{12} & 0 & 0 \\ 0 & 0 & 0 \end{matrix}$
$m\ (m \perp X_2)$ 2 comp., 1 inv.	$\begin{matrix} 0 & B_{12} & 0 \\ -B_{12} & 0 & B_{23} \\ 0 & -B_{23} & 0 \end{matrix}$		

In classes $\bar{1}$, $2/m$, 222, mmm, $\bar{3}$, 32, $\bar{3}m$, $\bar{4}$, $4/m$, 422, $\bar{4}2m$, $4/mmm$, $\bar{6}$, $6/m$, 622, $\bar{6}m2$, $6/mmm$, 23, $m3$, 432, $\bar{4}3m$, $m3m$, ∞/m, $\infty 2$, ∞/mm, $\infty\infty$, $\infty\infty m$ $\mathbf{B} = 0$.

Table E.9

εV^2—Second-Rank Pseudotensor D

Classes	D_{ij}	Classes	D_{ij}	Classes	D_{ij}
1 9 comp., 6 inv.	$\begin{matrix} D_{11} & D_{12} & D_{31} \\ D_{21} & D_{22} & D_{32} \\ D_{31} & D_{32} & D_{33} \end{matrix}$	222 3 comp.	$\begin{matrix} D_{11} & 0 & 0 \\ 0 & D_{22} & 0 \\ 0 & 0 & D_{33} \end{matrix}$	3, 4, 6, ∞ 3 comp.	$\begin{matrix} D_{11} & D_{12} & 0 \\ -D_{12} & D_{11} & 0 \\ 0 & 0 & D_{33} \end{matrix}$
2 $(2 \parallel X_2)$ 5 comp., 4 inv.	$\begin{matrix} D_{11} & 0 & D_{13} \\ 0 & D_{22} & 0 \\ D_{31} & 0 & D_{33} \end{matrix}$	$mm2$ 2 comp.	$\begin{matrix} 0 & D_{12} & 0 \\ D_{21} & 0 & 0 \\ 0 & 0 & 0 \end{matrix}$	32, 422 622, $\infty 2$ 2 comp.	$\begin{matrix} D_{11} & 0 & 0 \\ 0 & D_{11} & 0 \\ 0 & 0 & D_{33} \end{matrix}$
2 $(2 \parallel X_3)$ 5 comp., 4 inv.	$\begin{matrix} D_{11} & D_{12} & 0 \\ D_{21} & D_{22} & 0 \\ 0 & 0 & D_{33} \end{matrix}$	4 2 comp., 1 inv.	$\begin{matrix} D_{11} & D_{12} & 0 \\ D_{12} & -D_{11} & 0 \\ 0 & 0 & 0 \end{matrix}$	$3m$, $4mm$ $6mm$, ∞m 1 comp.	$\begin{matrix} 0 & D_{12} & 0 \\ -D_{12} & 0 & 0 \\ 0 & 0 & 0 \end{matrix}$
m $(m \perp X_2)$ 4 comp., 3 inv.	$\begin{matrix} 0 & D_{12} & 0 \\ D_{21} & 0 & D_{23} \\ 0 & D_{32} & 0 \end{matrix}$	$42m$ 1 comp.	$\begin{matrix} D_{11} & 0 & 0 \\ 0 & -D_{11} & 0 \\ 0 & 0 & 0 \end{matrix}$	23, 432, $\infty\infty$ 1 comp.	$\begin{matrix} D_{11} & 0 & 0 \\ 0 & D_{11} & 0 \\ 0 & 0 & D_{11} \end{matrix}$
m $(m \perp X_3)$ 4 comp., 3 inv.	$\begin{matrix} 0 & 0 & D_{13} \\ 0 & 0 & D_{23} \\ D_{31} & D_{32} & 0 \end{matrix}$				

In classes $\bar{1}$, $2/m$, mmm, $\bar{3}$, $\bar{3}m$, $4/m$, $4/mmm$, $\bar{6}$, $6/m$, $\bar{6}m2$, $6/mmm$, $m3$, $\bar{4}3m$, $m3m$, ∞/m, ∞/mm, $\infty\infty m$ pseudotensor $\mathbf{D} = 0$.

Table E.10

[V^3]—Third-Rank Tensor f Symmetric with Respect to All Indices

Classes	f_{ijk}
1 10 comp., 7 inv.	f_{111} f_{122} f_{133} f_{123} f_{211} f_{222} f_{233} f_{311} f_{322} f_{333}
2 $(2 \parallel X_2)$ 4 comp., 3 inv.	0 0 0 f_{123} f_{211} f_{222} f_{233} 0 0 0
2 $(2 \parallel X_3)$ 4 comp., 3 inv.	0 0 0 f_{123} 0 0 0 f_{311} f_{322} f_{333}
m $(m \perp X_2)$ 6 comp., 5 inv.	f_{111} f_{122} f_{133} 0 0 0 0 f_{311} f_{322} f_{333}
m $(m \perp X_3)$ 6 comp., 5 inv.	f_{111} f_{122} f_{133} 0 f_{211} f_{222} f_{233} 0 0 0
222, $\bar{4}2m$ 23 $\bar{4}3m$ 1 comp.	0 0 0 f_{123} 0 0 0 0 0 0

Classes	f_{ijk}
$mm2$ 3 comp.	0 0 0 0 0 0 0 f_{311} f_{322} f_{333}
$mm2$ $(\subset \bar{4}2m)$ 3 comp.	0 0 0 f_{123} 0 0 0 f_{311} f_{311} f_{333}
3 4 comp., 3 inv.	f_{111} $-f_{111}$ 0 0 $-f_{222}$ f_{222} 0 f_{311} f_{311} f_{333}
32, $\bar{6}2m$ $(2 \parallel X_1)$ 1 comp.	f_{111} $-f_{111}$ 0 0 0 0 0 0 0 0
$3m$ $(m \perp X_1)$ 3 comp.	0 0 0 0 $-f_{222}$ f_{222} 0 f_{311} f_{311} f_{333}
$3m$ $(m \perp X_2)$ 3 comp.	f_{111} $-f_{111}$ 0 0 0 0 0 f_{311} f_{311} f_{333}

Classes	f_{ijk}
4, 6, ∞, $4mm$, $6mm$, ∞m 2 comp.	0 0 0 0 0 0 0 f_{311} f_{311} f_{333}
$\bar{4}$ 2 comp., 1 inv.	0 0 0 f_{123} 0 0 0 f_{311} $-f_{311}$ 0
$4m2$ $(m \perp X_1)$ 1 comp.	0 0 0 0 0 0 0 f_{311} $-f_{311}$ 0
$\bar{6}$ 2 comp., 1 inv.	f_{111} $-f_{111}$ 0 0 $-f_{222}$ f_{222} 0 0 0 0
$\bar{6}m2$ $(m \perp X_1)$, 32 $(2 \parallel X_2)$ 1 comp.	0 0 0 0 $-f_{222}$ f_{222} 0 0 0 0

In classes $\bar{1}$, $2/m$, mmm, $\bar{3}$, $\bar{3}m$, $4/m$, 422, $4/mmm$, $6/m$, 622, $6/mmm$, $m3$, 432, $m3m$, ∞/m, $\infty 2$, ∞/mm, $\infty\infty$, $\infty\infty m$ $f = 0$.

Table E.11

$V[V^2]$—Third-Rank Tensor e Symmetric with Respect to Two Indices

$$e_{ilk} = e_{ikl}$$

Coefficients $e_{i\mu}$ connected with the components e_{ikl} by the recalculation rules

$$e_{i\mu} - e_{ikl} \quad (kl \leftrightarrow \mu = 1, \ldots, 6)$$

are written out.

In those cases when for the coefficients $d_{i\mu}$ connected with the tensor components d_{ikl} by the recalculation rules

$$d_{i\mu} = \begin{cases} d_{ikl} & (kl \leftrightarrow \mu = 1, 2, 3), \\ 2d_{ikl} & (kl \leftrightarrow \mu = 4, 5, 6), \end{cases}$$

the tables of coefficients have another form, coefficients $d_{i\mu}$ are also written out.

Classes	$e_{i\mu}$ and $d_{i\mu}$	Classes	$e_{i\mu}$ and $d_{i\mu}$
1 18 comp., 15 inv.	e_{11} e_{12} e_{13} e_{14} e_{15} e_{16} e_{21} e_{22} e_{23} e_{24} e_{25} e_{26} e_{31} e_{32} e_{33} e_{34} e_{35} e_{36}	$mm2$ $(\subset \bar{4}2m)$ 5 comp.	0 0 0 e_{14} e_{15} 0 0 0 0 e_{15} e_{14} 0 e_{31} e_{31} e_{33} 0 0 e_{36}
2 $(2 \parallel X_2)$ 8 comp., 7 inv.	0 0 0 e_{14} 0 e_{16} e_{21} e_{22} e_{23} 0 e_{25} 0 0 0 0 e_{34} 0 e_{36}	3 6 comp. 5 inv.	e_{11} $-e_{11}$ 0 e_{14} e_{15} $-e_{22}$ $-e_{22}$ e_{22} 0 e_{15} $-e_{14}$ $-e_{11}$ e_{31} e_{31} e_{33} 0 0 0
2 $(2 \parallel X_3)$ 8 comp., 7 inv.	0 0 0 e_{14} e_{15} 0 0 0 0 e_{24} e_{25} 0 e_{31} e_{32} e_{33} 0 0 e_{36}		d_{11} $-d_{11}$ 0 d_{14} d_{15} $-2d_{22}$ $-d_{22}$ d_{22} 0 d_{15} $-d_{14}$ $-2d_{11}$ d_{31} d_{31} d_{33} 0 0 0
m $(m \perp X_2)$ 10 comp., 9 inv.	e_{11} e_{12} e_{13} 0 e_{15} 0 0 0 0 e_{24} 0 e_{26} e_{31} e_{32} e_{33} 0 e_{35} 0	32 $(2 \parallel X_1)$ 2 comp.	e_{11} $-e_{11}$ 0 e_{14} 0 0 0 0 0 0 $-e_{14}$ $-e_{11}$ 0 0 0 0 0 0
m $(m \perp X_3)$ 10 comp., 9 inv.	e_{11} e_{12} e_{13} 0 0 e_{16} e_{21} e_{22} e_{23} 0 0 e_{26} 0 0 0 e_{31} e_{35} 0		d_{11} $-d_{11}$ 0 d_{14} 0 0 0 0 0 0 $-d_{14}$ $-2d_{11}$ 0 0 0 0 0 0
222 3 comp.	0 0 0 e_{14} 0 0 0 0 0 0 e_{25} 0 0 0 0 0 0 e_{36}	32 $(2 \parallel X_2)$ 2 comp.	0 0 0 e_{14} 0 $-e_{22}$ $-e_{22}$ e_{22} 0 0 $-e_{14}$ 0 0 0 0 0 0 0
$mm2$ 5 comp.	0 0 0 0 e_{15} 0 0 0 0 e_{24} 0 0 e_{31} e_{32} e_{33} 0 0 0		0 0 0 d_{14} 0 $-2d_{22}$ $-d_{22}$ d_{22} 0 0 $-d_{14}$ 0 0 0 0 0 0 0

Table E.11 (cont'd)

Classes	$e_{i\mu}$ and $d_{i\mu}$
$3m$ ($m \perp X_1$) 4 comp.	$\begin{matrix} 0 & 0 & 0 & 0 & e_{15} & -e_{22} \\ -e_{22} & e_{22} & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{matrix}$
	$\begin{matrix} 0 & 0 & 0 & 0 & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{matrix}$
$3m$ ($m \perp X_2$) 4 comp.	$\begin{matrix} e_{11} & -e_{11} & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & -e_{11} \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{matrix}$
	$\begin{matrix} d_{11} & -d_{11} & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & -2d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{matrix}$
4, 6, ∞ 4 comp.	$\begin{matrix} 0 & 0 & 0 & e_{14} & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & -e_{14} & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{matrix}$
422, 622, $\infty 2$ 1 comp.	$\begin{matrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
$4mm$, $6mm$ ∞m 3 comp.	$\begin{matrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{matrix}$
4 4 comp., 3 inv.	$\begin{matrix} 0 & 0 & 0 & e_{14} & e_{15} & 0 \\ 0 & 0 & 0 & -e_{15} & e_{14} & 0 \\ e_{31} & -e_{31} & 0 & 0 & 0 & e_{36} \end{matrix}$
$42m$ ($2 \parallel X_1$) 2 comp.	$\begin{matrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{36} \end{matrix}$

Classes	$e_{i\mu}$ and $d_{i\mu}$
$\bar{4}m2$ ($m \perp X_1$) 2 comp.	$\begin{matrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & -e_{15} & 0 & 0 \\ e_{31} & -e_{31} & 0 & 0 & 0 & 0 \end{matrix}$
$\bar{6}$ 2 comp., 1 inv.	$\begin{matrix} e_{11} & -e_{11} & 0 & 0 & 0 & -e_{22} \\ -e_{22} & e_{22} & 0 & 0 & 0 & -e_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
	$\begin{matrix} d_{11} & -d_{11} & 0 & 0 & 0 & -2d_{22} \\ -d_{22} & d_{22} & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
$\bar{6}m2$ ($m \perp X_1$) 1 comp.	$\begin{matrix} 0 & 0 & 0 & 0 & 0 & -e_{22} \\ -e_{22} & e_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
	$\begin{matrix} 0 & 0 & 0 & 0 & 0 & -2d_{22} \\ -d_{22} & d_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
$\bar{6}2m$ ($2 \parallel X_1$) 1 comp.	$\begin{matrix} e_{11} & -e_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -e_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
	$\begin{matrix} d_{11} & -d_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
$\bar{4}3m$, 23 1 comp.	$\begin{matrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{14} \end{matrix}$

In classes $\bar{1}$, $2/m$, mmm, $\bar{3}$, $\bar{3}m$, $4/m$, $4/mmm$, $6/m$, $6/mmm$, $m3$, 432, $m3m$, ∞/m, ∞/mm, $\infty\infty$, $\infty\infty m$ these tensors are zero.

Table E.12

$\{V^2\}V$ — Third-Rank Tensor γ Antisymmetric with Respect to Two Indices

$$\gamma_{jik} = -\gamma_{ijk}$$

Classes	γ_{ijk}	Classes	γ_{ijk}	Classes	γ_{ijk}
1 9 comp., 6 inv.	$\begin{matrix} \gamma_{231} & \gamma_{232} & \gamma_{233} \\ \gamma_{311} & \gamma_{312} & \gamma_{313} \\ \gamma_{121} & \gamma_{122} & \gamma_{123} \end{matrix}$	222 3 comp.	$\begin{matrix} \gamma_{231} & 0 & 0 \\ 0 & \gamma_{312} & 0 \\ 0 & 0 & \gamma_{123} \end{matrix}$	32, 422, 622, $\infty 2$ 2 comp.	$\begin{matrix} \gamma_{231} & 0 & 0 \\ 0 & \gamma_{231} & 0 \\ 0 & 0 & \gamma_{123} \end{matrix}$
2 $(2 \parallel X_2)$ 5 comp., 4 inv.	$\begin{matrix} \gamma_{231} & 0 & \gamma_{233} \\ 0 & \gamma_{312} & 0 \\ \gamma_{121} & 0 & \gamma_{123} \end{matrix}$	$mm2$ 2 comp.	$\begin{matrix} 0 & \gamma_{232} & 0 \\ \gamma_{311} & 0 & 0 \\ 0 & 0 & 0 \end{matrix}$	$3m$, $4mm$, $6mm$, ∞m 1 comp.	$\begin{matrix} 0 & \gamma_{232} & 0 \\ -\gamma_{232} & 0 & 0 \\ 0 & 0 & 0 \end{matrix}$
2 $(2 \parallel X_3)$ 5 comp., 4 inv.	$\begin{matrix} \gamma_{231} & \gamma_{232} & 0 \\ \gamma_{311} & \gamma_{312} & 0 \\ 0 & 0 & \gamma_{123} \end{matrix}$	4 2 comp., 1 inv.	$\begin{matrix} \gamma_{231} & \gamma_{232} & 0 \\ \gamma_{232} & -\gamma_{231} & 0 \\ 0 & 0 & 0 \end{matrix}$	23, 432, $\infty\infty$ 1 comp.	$\begin{matrix} \gamma_{123} & 0 & 0 \\ 0 & \gamma_{123} & 0 \\ 0 & 0 & \gamma_{123} \end{matrix}$
m $(m \perp X_2)$ 4 comp., 3 inv.	$\begin{matrix} 0 & \gamma_{232} & 0 \\ \gamma_{311} & 0 & \gamma_{313} \\ 0 & \gamma_{122} & 0 \end{matrix}$	$\bar{4}2m$ 1 comp.	$\begin{matrix} \gamma_{231} & 0 & 0 \\ 0 & -\gamma_{231} & 0 \\ 0 & 0 & 0 \end{matrix}$		
m $(m \perp X_3)$ 4 comp., 3 inv.	$\begin{matrix} 0 & 0 & \gamma_{233} \\ 0 & 0 & \gamma_{313} \\ \gamma_{121} & \gamma_{122} & 0 \end{matrix}$	3, 4, 6, ∞ 3 comp.	$\begin{matrix} \gamma_{231} & \gamma_{232} & 0 \\ -\gamma_{232} & \gamma_{231} & 0 \\ 0 & 0 & \gamma_{123} \end{matrix}$		

In classes $\bar{1}$, $2/m$, mmm, $\bar{3}$, $\bar{3}m$, $4/m$, $4/mmm$, $\bar{6}$, $6/m$, $\bar{6}m2$, $6/mmm$, $m3$, $\bar{4}3m$, $m3m$, ∞/m, ∞/mm, $\infty\infty m$ $\gamma = 0$.

Table E.13

V^3 — Third-Rank Tensor β

Classes	β_{ijk}
1 27 comp., 24 inv.	$\begin{matrix} \beta_{111} & \beta_{122} & \beta_{133} & \beta_{123} & \beta_{131} & \beta_{112} & \beta_{132} & \beta_{113} & \beta_{121} \\ \beta_{211} & \beta_{222} & \beta_{233} & \beta_{223} & \beta_{231} & \beta_{212} & \beta_{232} & \beta_{213} & \beta_{221} \\ \beta_{311} & \beta_{322} & \beta_{333} & \beta_{323} & \beta_{331} & \beta_{312} & \beta_{332} & \beta_{313} & \beta_{321} \end{matrix}$
2 $(2 \parallel X_2)$ 13 comp., 12 inv.	$\begin{matrix} 0 & 0 & 0 & \beta_{123} & 0 & \beta_{112} & \beta_{132} & 0 & \beta_{121} \\ \beta_{211} & \beta_{222} & \beta_{233} & 0 & \beta_{231} & 0 & 0 & \beta_{213} & 0 \\ 0 & 0 & 0 & \beta_{323} & 0 & \beta_{312} & \beta_{332} & 0 & \beta_{321} \end{matrix}$
2 $(2 \parallel X_3)$ 13 comp., 12 inv.	$\begin{matrix} 0 & 0 & 0 & \beta_{123} & \beta_{131} & 0 & \beta_{132} & \beta_{113} & 0 \\ 0 & 0 & 0 & \beta_{223} & \beta_{231} & 0 & \beta_{232} & \beta_{213} & 0 \\ \beta_{311} & \beta_{322} & \beta_{333} & 0 & 0 & \beta_{312} & 0 & 0 & \beta_{321} \end{matrix}$

***Table E.13** (cont'd)*

Classes	β_{ijk}
m $(m \perp X_2)$ 14 comp., 13 inv.	β_{111} β_{122} β_{133} 0 β_{131} 0 0 β_{113} 0 0 0 0 β_{223} 0 β_{212} β_{232} 0 β_{221} β_{311} β_{322} β_{333} 0 β_{331} 0 0 β_{313} 0
m $(m \perp X_3)$ 14 comp., 13 inv.	β_{111} β_{122} β_{133} 0 0 β_{112} 0 0 β_{121} β_{211} β_{222} β_{233} 0 0 β_{212} 0 0 β_{221} 0 0 0 β_{323} β_{331} 0 β_{332} β_{313} 0
222 6 comp.	0 0 0 β_{123} 0 0 β_{132} 0 0 0 0 0 0 β_{231} 0 0 β_{213} 0 0 0 0 0 0 β_{312} 0 0 β_{321}
$mm2$ 7 comp	0 0 0 0 β_{131} 0 0 β_{113} 0 0 0 0 β_{223} 0 0 β_{232} 0 0 β_{311} β_{322} β_{333} 0 0 0 0 0 0
3 9 comp., 8 inv	β_{111} $-\beta_{111}$ 0 β_{123} β_{131} $-\beta_{222}$ $-\beta_{231}$ β_{223} $-\beta_{222}$ $-\beta_{222}$ β_{222} 0 β_{223} β_{231} $-\beta_{111}$ β_{131} $-\beta_{123}$ $-\beta_{111}$ β_{311} β_{311} β_{333} 0 0 β_{312} 0 0 $-\beta_{312}$
32 $(2 \parallel X_1)$ 4 comp.	β_{111} $-\beta_{111}$ 0 β_{123} 0 0 $-\beta_{231}$ 0 0 0 0 0 0 β_{231} $-\beta_{111}$ 0 $-\beta_{123}$ $-\beta_{111}$ 0 0 0 0 0 β_{312} 0 0 $-\beta_{312}$
$3m$ $(m \perp X_1)$ 5 comp.	0 0 0 0 β_{131} $-\beta_{222}$ 0 β_{223} $-\beta_{222}$ $-\beta_{222}$ β_{222} 0 β_{223} 0 0 β_{131} 0 0 β_{311} β_{311} β_{333} 0 0 0 0 0 0
4, 6, ∞ 7 comp.	0 0 0 β_{123} β_{131} 0 $-\beta_{231}$ β_{223} 0 0 0 0 β_{223} β_{231} 0 β_{131} $-\beta_{123}$ 0 β_{311} β_{311} β_{333} 0 0 β_{312} 0 0 $-\beta_{312}$
422, 622, $\infty 2$ 3 comp.	0 0 0 β_{123} 0 0 $-\beta_{231}$ 0 0 0 0 0 0 β_{231} 0 0 $-\beta_{123}$ 0 0 0 0 0 0 β_{312} 0 0 $-\beta_{312}$

Table E.13 (cont'd)

Classes	β_{ijk}
$4mm$, $6mm$ ∞m 4 comp.	$\begin{matrix} 0 & 0 & 0 & 0 & \beta_{131} & 0 & 0 & \beta_{223} & 0 \\ 0 & 0 & 0 & \beta_{223} & 0 & 0 & \beta_{131} & 0 & 0 \\ \beta_{311} & \beta_{311} & \beta_{333} & 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
$\bar{4}$ 6 comp., 5 inv.	$\begin{matrix} 0 & 0 & 0 & \beta_{123} & \beta_{131} & 0 & \beta_{231} & -\beta_{223} & 0 \\ 0 & 0 & 0 & \beta_{223} & \beta_{231} & 0 & -\beta_{131} & \beta_{123} & 0 \\ \beta_{311} & -\beta_{311} & 0 & 0 & 0 & \beta_{312} & 0 & 0 & \beta_{312} \end{matrix}$
$\bar{4}2m$ 3 comp.	$\begin{matrix} 0 & 0 & 0 & \beta_{123} & 0 & 0 & \beta_{231} & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_{231} & 0 & 0 & \beta_{123} & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_{312} & 0 & 0 & \beta_{312} \end{matrix}$
$\bar{6}$ 2 comp., 1 inv.	$\begin{matrix} \beta_{111} & -\beta_{111} & 0 & 0 & 0 & -\beta_{222} & 0 & 0 & -\beta_{222} \\ -\beta_{222} & \beta_{222} & 0 & 0 & 0 & -\beta_{111} & 0 & 0 & -\beta_{111} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
$\bar{6}m2$ $(m \perp X_1)$ 1 comp.	$\begin{matrix} 0 & 0 & 0 & 0 & 0 & -\beta_{222} & 0 & 0 & -\beta_{222} \\ -\beta_{222} & \beta_{222} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
$\bar{6}2m$ $(2 \parallel X_1)$ 1 comp.	$\begin{matrix} \beta_{111} & -\beta_{111} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\beta_{111} & 0 & 0 & -\beta_{111} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$
23 2 comp.	$\begin{matrix} 0 & 0 & 0 & \beta_{123} & 0 & 0 & \beta_{321} & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_{123} & 0 & 0 & \beta_{321} & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_{123} & 0 & 0 & \beta_{321} \end{matrix}$
$\bar{4}3m$ 1 comp.	$\begin{matrix} 0 & 0 & 0 & \beta_{123} & 0 & 0 & \beta_{123} & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_{123} & 0 & 0 & \beta_{123} & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_{123} & 0 & 0 & \beta_{123} \end{matrix}$
432, $\infty\infty$ 1 comp.	$\begin{matrix} 0 & 0 & 0 & \beta_{123} & 0 & 0 & -\beta_{123} & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_{123} & 0 & 0 & -\beta_{123} & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_{123} & 0 & 0 & -\beta_{123} \end{matrix}$

In classes $\bar{1}$, $2/m$, mmm, $\bar{3}$, $\bar{3}m$, $4/m$, $4/mmm$, $6/m$, $6/mmm$, $m3$, $m3m$, ∞/m, ∞/mm, $\infty\infty m$ $\beta = 0$.

$\varepsilon V[V^2]$—Third-Rank Pseudotensor A Symmetric with Respect to Two Indices

$$A_{ilk} = A_{ikl}$$

Coefficients $A_{i\mu}$ connected with the components A_{ikl} by the recalculation rules

$$A_{i\mu} = A_{ikl} \quad (kl \leftrightarrow \mu = 1, \ldots, 6)$$

are written out

Classes	$A_{i\mu}$	Classes	$A_{i\mu}$
$1, \bar{1}$ 18 comp., 15 inv.	A_{11} A_{12} A_{13} A_{14} A_{15} A_{16} A_{21} A_{22} A_{23} A_{24} A_{25} A_{26} A_{31} A_{32} A_{33} A_{34} A_{35} A_{36}	$32, 3m, \bar{3}m$ $(2 \parallel X_1, m \perp X_1)$ 2 comp.	A_{11} $-A_{11}$ 0 A_{14} 0 0 0 0 0 0 $-A_{14}$ $-A_{11}$ 0 0 0 0 0 0
$2, m, 2/m$ $(2 \parallel X_2, m \perp X_2)$ 8 comp., 7 inv.	0 0 0 A_{14} 0 A_{16} A_{21} A_{22} A_{23} 0 A_{25} 0 0 0 0 A_{34} 0 A_{16}	$4, \bar{4}, 4/m,$ $6, \bar{6}, 6/m,$ $\infty, \infty/m$ 4 comp.	0 0 0 A_{14} A_{15} 0 0 0 0 A_{15} $-A_{14}$ 0 A_{31} A_{31} A_{33} 0 0 0
$2, m, 2/m$ $(2 \parallel X_3, m \perp X_3)$ 8 comp., 7 inv.	0 0 0 A_{14} A_{15} 0 0 0 0 A_{24} A_{25} 0 A_{31} A_{32} A_{33} 0 0 A_{36}	$422, 4mm$ $\bar{4}2m,$ $4/mmm,$ $622, 6mm,$ $\bar{6}m2,$ $6/mmm,$ $\infty 2, \infty m,$ ∞/mm 1 comp.	0 0 0 A_{14} 0 0 0 0 0 0 $-A_{14}$ 0 0 0 0 0 0 0
$222,$ $mm2,$ mmm 3 comp.	0 0 0 A_{14} 0 0 0 0 0 0 A_{25} 0 0 0 0 0 0 A_{36}	$23, m3$ 1 comp.	0 0 0 A_{14} 0 0 0 0 0 0 A_{14} 0 0 0 0 0 0 A_{14}
$3, \bar{3}$ 6 comp., 5 inv.	A_{11} $-A_{11}$ 0 A_{14} A_{15} $-A_{22}$ $-A_{22}$ A_{22} 0 A_{15} $-A_{14}$ $-A_{11}$ A_{31} A_{31} A_{33} 0 0 0		

In classes $432, \bar{4}3m, m3m, \infty\infty, \infty\infty m$ $A = 0$.

Table E.15

$\varepsilon\{V^2\}V$—Third-Rank Pseudotensor ψ Antisymmetric with Respect to Two Indices

$$\psi_{jik} = -\psi_{ijk}$$

Classes	ψ_{ijk}	Classes	ψ_{ijk}
$1, \bar{1}$ 9 comp., 6 inv.	ψ_{231} ψ_{232} ψ_{233} ψ_{311} ψ_{312} ψ_{313} ψ_{121} ψ_{122} ψ_{123}	$2, m, 2/m$ $(2 \parallel X_2, m \perp X_2)$ 5 comp., 4 inv.	ψ_{231} 0 ψ_{233} 0 ψ_{312} 0 ψ_{121} 0 ψ_{123}

Table E.15 (cont'd)

Classes	ψ_{ijk}	Classes	ψ_{ijk}
2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$) 5 comp., 4 inv.	ψ_{231} ψ_{232} 0 ψ_{311} ψ_{312} 0 0 0 ψ_{123}	32, $3m$, $\bar{3}m$, 422, $4mm$, $\bar{4}2m$, $4/mmm$, 622, $6mm$, $\bar{6}m2$, $6/mmm$, $\infty 2$, ∞m, ∞/mm 2 comp.	ψ_{231} 0 0 0 ψ_{231} 0 0 0 ψ_{123}
222, $mm2$, mmm 3 comp.	ψ_{231} 0 0 0 ψ_{312} 0 0 0 ψ_{123}		
3, $\bar{3}$, 4, $\bar{4}$, $4/m$, 6, $\bar{6}$, $6/m$ ∞, ∞/m 3 comp.	ψ_{231} ψ_{232} 0 $-\psi_{232}$ ψ_{231} 0 0 0 ψ_{123}	23, $m3$, 432, $\bar{4}3m$, $m3m$, $\infty\infty\infty$, $\infty\infty\infty m$ 1 comp.	ψ_{123} 0 0 0 ψ_{123} 0 0 0 ψ_{123}

Table E.16

[V^4]—Fourth-Rank Tensor l Symmetric with Respect to All Indices

Classes	l_{ijmn}	Classes	l_{ijmn}
1, $\bar{1}$ 15 comp., 12 inv.	l_{1111} l_{1222} l_{1333} l_{2233} l_{1123} l_{2111} l_{2222} l_{2333} l_{3311} l_{2213} l_{3111} l_{3222} l_{3333} l_{1122} l_{3312}	4, $\bar{4}$, $4/m$ 5 comp., 4 inv.	l_{1111} $-l_{2111}$ 0 l_{2233} 0 l_{2111} l_{1111} 0 l_{2233} 0 0 0 l_{3333} l_{1122} 0
2, m, $2/m$ ($2 \parallel X_2$, $m \perp X_2$) 9 comp., 8 inv.	l_{1111} 0 l_{1333} l_{2233} 0 0 l_{2222} 0 l_{3311} l_{2213} l_{3111} 0 l_{3333} l_{1122} 0	422,, $4mm$, $\bar{4}2m$ $4/mmm$ 4 comp.	l_{1111} 0 0 l_{2233} 0 0 l_{1111} 0 l_{2233} 0 0 0 l_{3333} l_{1122} 0
2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$) 9 comp., 8 inv.	l_{1111} l_{1222} 0 l_{2233} 0 l_{2111} l_{2222} 0 l_{3311} 0 0 0 l_{3333} l_{1122} l_{3312}	6, $\bar{6}$, $6/m$, 622, $6mm$, $\bar{6}m2$, $6/mmm$ ∞, ∞/m, $\infty 2$, ∞m, ∞/mm 3 comp.	$3l_{1122}$ 0 0 l_{2233} 0 0 $3l_{1122}$ 0 l_{2233} 0 0 0 l_{3333} l_{1122} 0
222, $mm2$, mmm 6 comp.	l_{1111} 0 0 l_{2233} 0 0 l_{2222} 0 l_{3311} 0 0 0 l_{3333} l_{1122} 0		
3, $\bar{3}$ 5 comp., 4 inv.	$3l_{1122}$ 0 0 l_{2233} l_{1123} 0 $3l_{1122}$ 0 l_{2233} $-l_{3111}$ l_{3111} $-l_{1123}$ l_{3333} l_{1122} 0	23, $m3$, 432, $\bar{4}3m$, $m3m$ 2 comp.	l_{1111} 0 0 l_{2233} 0 0 l_{1111} 0 l_{2233} 0 0 0 l_{1111} l_{2233} 0
32, $3m$, $\bar{3}m$ 4 comp.	$3l_{1122}$ 0 0 l_{2233} l_{1123} 0 $3l_{1122}$ 0 l_{2233} 0 0 $-l_{1123}$ l_{3333} l_{1122} 0	$\infty\infty$, $\infty\infty m$ 1 comp.	$3l_{2233}$ 0 0 l_{2233} 0 0 $3l_{2233}$ 0 l_{2233} 0 0 0 $3l_{2233}$ l_{2233} 0

Table E.17

$V[V^3]$—Fourth-Rank Tensor k Symmetric with Respect to the Last Three Indices

Classes	k_{ijmn}									
1, $\bar{1}$ 30 comp., 27 inv.	k_{1111} k_{2111} k_{3111}	k_{1222} k_{2222} k_{3222}	k_{1333} k_{2333} k_{3333}	k_{1122} k_{2122} k_{3122}	k_{1233} k_{2233} k_{3233}	k_{1311} k_{2311} k_{3311}	k_{1133} k_{2133} k_{3133}	k_{1211} k_{2211} k_{3211}	k_{1322} k_{2322} k_{3322}	k_{1123} k_{2123} k_{3123}
2, m, $2/m$ ($2 \parallel X_2$, $m \perp X_2$) 16 comp., 15 inv.	k_{1111} 0 k_{3111}	0 k_{2222} 0	k_{1333} 0 k_{3333}	k_{1122} 0 k_{3122}	0 k_{2233} 0	k_{1311} 0 k_{3311}	k_{1133} 0 k_{3133}	0 k_{2211} 0	k_{1322} 0 k_{3322}	0 k_{2123} 0
2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$) 16 comp., 15 inv.	k_{1111} k_{2111} 0	k_{1222} k_{2222} 0	0 0 k_{3333}	k_{1122} k_{2122} 0	k_{1233} k_{2233} 0	0 0 k_{3311}	k_{1133} k_{2133} 0	k_{1211} k_{2211} 0	0 0 k_{3322}	0 0 k_{3123}
222, $mm2$, mmm 9 comp.	k_{1111} 0 0	0 k_{2222} 0	0 0 k_{3333}	k_{1122} 0 0	0 k_{2233} 0	0 0 k_{3311}	k_{1133} 0 0	0 k_{2211} 0	0 0 k_{3322}	0 0 0
3, $\bar{3}$ 10 comp., 9 inv.	$3k_{1122}$ $-3k_{1211}$ k_{3111}	$3k_{1211}$ $3k_{1122}$ $-k_{3211}$	0 0 k_{3333}	k_{1122} $-k_{1211}$ $-k_{3111}$	k_{1233} k_{2233} 0	k_{1311} k_{2311} k_{3311}	k_{2233} $-k_{1233}$ 0	k_{1211} k_{1122} k_{3211}	$-k_{1311}$ $-k_{2311}$ k_{3311}	k_{2311} $-k_{1311}$ k_{3123}
32, $3m$, $\bar{3}m$ 6 comp.	$3k_{1122}$ 0 0	0 $3k_{1122}$ $-k_{3211}$	0 0 k_{3333}	k_{1122} 0 0	0 k_{2233} 0	0 k_{2311} k_{3311}	k_{2233} 0 0	0 k_{1122} k_{3211}	0 $-k_{2311}$ k_{3311}	k_{2311} 0 0
4, 4, $4/m$ 8 comp 7 inv.	k_{1111} k_{2111} 0	$-k_{2111}$ k_{1111} 0	0 0 k_{3333}	k_{1122} $-k_{1211}$ 0	k_{1233} k_{2233} 0	0 0 k_{3311}	k_{2233} $-k_{1233}$ 0	k_{1211} k_{1122} 0	0 0 k_{3311}	0 0 k_{3123}
422, $4mm$, $\bar{4}2m$, $4/mmm$ 5 comp.	k_{1111} 0 0	0 k_{1111} 0	0 0 k_{3333}	k_{1122} 0 0	0 k_{2233} 0	0 0 k_{3311}	k_{2233} 0 0	0 k_{1122} 0	0 0 k_{3311}	0 0 0
6, $\bar{6}$, $6/m$, ∞, ∞/m 6 comp.	$3k_{1122}$ $-3k_{1211}$ 0	$3k_{1211}$ $3k_{1122}$ 0	0 0 k_{3333}	k_{1122} $-k_{1211}$ 0	k_{1233} k_{2233} 0	0 0 k_{3311}	k_{2233} $-k_{1233}$ 0	k_{1211} k_{1122} 0	0 0 k_{3311}	0 0 k_{3123}

Table E.17 (cont'd)

Classes	$kijmn$									
622, $6mm$ $\bar{6}m2$, $6/mmm$, $\infty 2$, ∞m, ∞/mm 4 comp.	$3k_{1122}$ 0 0	0 $3k_{1122}$ 0	0 0 k_{3333}	k_{1122} 0 0	0 k_{2233} 0	0 0 k_{3311}	k_{2233} 0 0	0 k_{1122} 0	0 0 k_{3311}	0 0 0
23, $m3$ 3 comp.	k_{1111} 0 0	0 k_{1111} 0	0 0 k_{1111}	k_{2233} 0 0	0 k_{2233} 0	0 0 k_{2233}	k_{3322} 0 0	0 k_{3322} 0	0 0 k_{3322}	0 0 0
432, $\bar{4}3m$, $m3m$ 2 comp.	k_{1111} 0 0	0 k_{1111} 0	0 0 k_{1111}	k_{2233} 0 0	0 k_{2233} 0	0 0 k_{2233}	k_{2233} 0 0	0 k_{2233} 0	0 0 k_{2233}	0 0 0
$\infty\infty$, $\infty\infty m$ 1 comp.	$3k_{2233}$ 0 0	0 $3k_{2233}$ 0	0 0 $3k_{2233}$	k_{2233} 0 0	0 k_{2233} 0	0 0 k_{2233}	k_{2233} 0 0	0 k_{2233} 0	0 0 k_{2233}	0 0 0

Table E.18

$[[V^2]^2]$ — Fourth-Rank Tensor c Symmetric with Respect to Two Pairs of Indices Under Permutations:

$$c_{ijkl} = c_{jikl} = c_{ijlk} = c_{klij}$$

Coefficients $c_{\lambda\mu}$ connected with the components c_{ijkl} by the recalculation rules

$$c_{\lambda\mu} = c_{ijkl} \quad (ij \leftrightarrow \lambda = 1, \ldots, 6; \quad kl \leftrightarrow \mu = 1, \ldots, 6)$$

are written out.

When for the coefficients $s_{\lambda\mu}$ connected with the components s_{ijkl} by the recalculation rules

$$s_{\lambda\mu} = \begin{cases} s_{ijkl} & (ij \leftrightarrow \lambda = 1, 2, 3; \quad kl \leftrightarrow \mu = 1, 2, 3), \\ 2s_{ijkl} & (ij \leftrightarrow \lambda = 1, 2, 3; \quad kl \leftrightarrow \mu = 4, 5, 6), \\ 2s_{ijkl} & (ij \leftrightarrow \lambda = 4, 5, 6; \quad kl \leftrightarrow \mu = 1, 2, 3), \\ 4s_{ijkl} & (ij \leftrightarrow \lambda = 4, 5, 6; \quad kl \leftrightarrow \mu = 4, 5, 6), \end{cases}$$

the tables have a different form, coefficients $s_{\lambda\mu}$ are also written out.

Classes	$c_{\lambda\mu}$ and $s_{\lambda\mu}$						Classes	$c_{\lambda\mu}$ and $s_{\lambda\mu}$					
1, $\bar{1}$ 21 comp., 18 inv.	c_{11}	c_{12} c_{22}	c_{13} c_{23} c_{33}	c_{14} c_{24} c_{34} c_{44}	c_{15} c_{25} c_{35} c_{45} c_{55}	c_{16} c_{26} c_{36} c_{46} c_{56} c_{66}	2, m, $2/m$ ($2 \parallel X_2$, $m \perp X_2$) 13 comp., 12 inv.	c_{11}	c_{12} c_{22}	c_{13} c_{23} c_{33}	0 0 0 c_{44}	c_{15} c_{25} c_{35} 0 c_{55}	0 0 0 c_{46} 0 c_{66}

Table E.18 (cont'd)

Classes	$c_{\lambda\mu}$ and $s_{\lambda\mu}$
2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$) 13 comp., 12 inv.	c_{11} c_{12} c_{13} 0 0 c_{16} c_{22} c_{23} 0 0 c_{26} c_{33} 0 0 c_{36} c_{44} c_{45} 0 c_{55} 0 c_{66}
222, $mm2$, mmm 9 comp.	c_{11} c_{12} c_{13} 0 0 0 c_{22} c_{23} 0 0 0 c_{33} 0 0 0 c_{44} 0 0 c_{55} 0 c_{66}
3, $\bar{3}$ 7 comp., 6 inv. *)	c_{11} c_{12} c_{13} c_{14} $-c_{25}$ 0 c_{11} c_{13} $-c_{14}$ c_{25} 0 c_{33} 0 0 0 c_{44} 0 c_{25} c_{44} c_{14} c_{66}
	s_{11} s_{12} s_{13} s_{14} $-s_{25}$ 0 s_{11} s_{13} $-s_{14}$ s_{25} 0 s_{33} 0 0 0 s_{44} 0 $2s_{25}$ s_{14} $2s_{14}$ s_{66}
32, $3m$, $\bar{3}m$ 6 comp. *)	c_{11} c_{12} c_{13} c_{14} 0 0 c_{11} c_{13} $-c_{14}$ 0 0 c_{33} 0 0 0 c_{44} 0 0 c_{44} c_{14} c_{66}
	s_{11} s_{12} s_{13} s_{14} 0 0 s_{11} s_{13} $-s_{14}$ 0 0 s_{33} 0 0 0 s_{44} 0 0 s_{44} $2s_{14}$ s_{66}
4, $\bar{4}$, $4/m$ 7 comp., 6 inv.	c_{11} c_{12} c_{13} 0 0 c_{16} c_{11} c_{13} 0 0 $-c_{16}$ c_{33} 0 0 0 c_{44} 0 0 c_{44} 0 c_{66}
422, $4mm$, $\bar{4}2m$, $4/mmm$ 6 comp. 6, $\bar{6}$, $6/m$, 622, $6mm$, $\bar{6}m2$, $6/mmm$, ∞, ∞/m, $\infty 2$, ∞m, ∞/mm 5 comp. *)	c_{11} c_{12} c_{13} 0 0 0 c_{11} c_{13} 0 0 0 c_{33} 0 0 0 c_{44} 0 0 c_{44} 0 c_{66}
23, $m3$, 432, $\bar{4}3m$, $m3m$ 3 comp. $\infty\infty$, $\infty\infty m$ 2 comp. **)	c_{11} c_{12} c_{12} 0 0 0 c_{11} c_{12} 0 0 0 c_{11} 0 0 0 c_{44} 0 0 c_{44} 0 c_{44}

*)In classes 3, $\bar{3}$, 32, $\bar{3}m$, $\bar{3}m$, 6, $\bar{6}$, $6/m$, 622, $6mm$, $\bar{6}m2$, $6/mmm$, ∞, ∞/m, $\infty 2$, ∞m, ∞/mm $c_{66} = \frac{1}{2}(c_{11} - c_{12})$, $s_{66} = 2(s_{11} - s_{12})$.

**)In classes $\infty\infty$ and $\infty\infty m$ $c_{44} = \frac{1}{2}(c_{11} - c_{12})$, $s_{44} = 2(s_{11} - s_{12})$

$[V^2]^2$ — Fourth-Rank Tensor p Symmetric with Respect to Two Pairs of Indices:

$$p_{ijkl} = p_{jikl} = p_{ijlk}$$

Coefficients $p_{\lambda\mu}$ connected with the components p_{ijkl} by the recalculation rules

$$p_{\lambda\mu} = p_{ijkl} \quad (ij \leftrightarrow \lambda = 1, \ldots, 6; \quad kl \leftrightarrow \mu = 1, \ldots, 6)$$

are written out.

When for the coefficients $\pi_{\lambda\mu}$ connected with the tensor components π_{ijkl} by the recalculation rules

$$\pi_{\lambda\mu} = \begin{cases} \pi_{ijkl} & (ij \leftrightarrow \lambda = 1, \ldots, 6; \quad kl \leftrightarrow \mu = 1, 2, 3), \\ 2\pi_{ijkl} & (ij \leftrightarrow \lambda = 1, \ldots, 6; \quad kl \leftrightarrow \mu = 4, 5, 6), \end{cases}$$

the tables have a different form, coefficients $\pi_{\lambda\mu}$ are also given.

Classes	$p_{\lambda\mu}$ and $\pi_{\lambda\mu}$	Classes	$p_{\lambda\mu}$ and $\pi_{\lambda\mu}$
1, $\bar{1}$ 36 comp., 33 inv.	$\begin{matrix} p_{11} & p_{12} & p_{13} & p_{14} & p_{15} & p_{16} \\ p_{21} & p_{22} & p_{23} & p_{24} & p_{25} & p_{26} \\ p_{31} & p_{32} & p_{33} & p_{34} & p_{35} & p_{36} \\ p_{41} & p_{42} & p_{43} & p_{44} & p_{45} & p_{46} \\ p_{51} & p_{52} & p_{53} & p_{54} & p_{55} & p_{56} \\ p_{61} & p_{62} & p_{63} & p_{64} & p_{65} & p_{66} \end{matrix}$	3, $\bar{3}$ 12 comp., 11 inv. *)	$\begin{matrix} p_{11} & p_{12} & p_{13} & p_{14} & -p_{25} & p_{16} \\ p_{12} & p_{11} & p_{13} & -p_{14} & p_{25} & -p_{16} \\ p_{31} & p_{31} & p_{33} & 0 & 0 & 0 \\ p_{41} & -p_{41} & 0 & p_{44} & p_{45} & p_{52} \\ -p_{52} & p_{52} & 0 & p_{45} & p_{44} & p_{41} \\ -p_{16} & p_{16} & 0 & p_{25} & p_{14} & p_{66} \end{matrix}$
2, m, $2/m$ $(2 \parallel X_2,$ $m \perp X_2)$ 20 comp., 19 inv.	$\begin{matrix} p_{11} & p_{12} & p_{13} & 0 & p_{15} & 0 \\ p_{21} & p_{22} & p_{23} & 0 & p_{25} & 0 \\ p_{31} & p_{32} & p_{33} & 0 & p_{35} & 0 \\ 0 & 0 & 0 & p_{44} & 0 & p_{46} \\ p_{51} & p_{52} & p_{53} & 0 & p_{55} & 0 \\ p_{61} & p_{62} & p_{63} & p_{64} & 0 & p_{66} \end{matrix}$		$\begin{matrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & \pi_{25} & 2\pi_{62} \\ \pi_{12} & \pi_{11} & \pi_{13} & -\pi_{14} & \pi_{25} & 2\pi_{62} \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ \pi_{41} & -\pi_{41} & 0 & \pi_{44} & \pi_{45} & 2\pi_{52} \\ -\pi_{52} & \pi_{52} & 0 & -\pi_{45} & \pi_{44} & 2\pi_{41} \\ -\pi_{62} & \pi_{62} & 0 & \pi_{25} & \pi_{14} & \pi_{66} \end{matrix}$
2, m, $2/m$ $(2 \parallel X_3,$ $m \perp X_3)$ 20 comp., 19 inv.	$\begin{matrix} p_{11} & p_{12} & p_{13} & 0 & 0 & p_{16} \\ p_{21} & p_{22} & p_{23} & 0 & 0 & p_{26} \\ p_{31} & p_{32} & p_{33} & 0 & 0 & p_{36} \\ 0 & 0 & 0 & p_{44} & p_{45} & 0 \\ 0 & 0 & 0 & p_{54} & p_{55} & 0 \\ p_{61} & p_{62} & p_{63} & 0 & 0 & p_{66} \end{matrix}$	32, $3m$ $\bar{3}m$ 8 comp. *)	$\begin{matrix} p_{11} & p_{12} & p_{13} & p_{14} & 0 & 0 \\ p_{12} & p_{11} & p_{13} & -p_{14} & 0 & 0 \\ p_{31} & p_{31} & p_{33} & 0 & 0 & 0 \\ p_{41} & -p_{41} & 0 & p_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & p_{44} & p_{41} \\ 0 & 0 & 0 & 0 & p_{14} & p_{66} \end{matrix}$
222, $mm2$, mmm 12 comp.	$\begin{matrix} p_{11} & p_{12} & p_{13} & 0 & 0 & 0 \\ p_{21} & p_{22} & p_{23} & 0 & 0 & 0 \\ p_{31} & p_{32} & p_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & p_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & p_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & p_{66} \end{matrix}$		$\begin{matrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & -\pi_{14} & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ \pi_{41} & -\pi_{41} & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 2\pi_{41} \\ 0 & 0 & 0 & 0 & \pi_{14} & \pi_{66} \end{matrix}$

Table E.19 (cont'd)

Classes	$p_{\lambda\mu}$ and $\pi_{\lambda\mu}$	Classes	$p_{\lambda\mu}$ and $\pi_{\lambda\mu}$
6, $\bar{6}$, $6/m$ ∞, ∞/m 8 comp. *)	$\begin{matrix} p_{11} & p_{12} & p_{13} & 0 & 0 & p_{16} \\ p_{12} & p_{11} & p_{13} & 0 & 0 & -p_{16} \\ p_{31} & p_{31} & p_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & p_{44} & p_{45} & 0 \\ 0 & 0 & 0 & -p_{45} & p_{44} & 0 \\ -p_{16} & p_{16} & 0 & 0 & 0 & p_{66} \end{matrix}$	422, $4mm$, $\bar{4}2m$, $4/mmm$ 7 comp. 622, $6mm$, $\bar{6}m2$, $6/mmm$, $\infty 2$, ∞m, ∞/mm 6 comp. *)	$\begin{matrix} p_{11} & p_{12} & p_{13} & 0 & 0 & 0 \\ p_{12} & p_{11} & p_{13} & 0 & 0 & 0 \\ p_{31} & p_{31} & p_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & p_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & p_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & p_{66} \end{matrix}$
	$\begin{matrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 2\pi_{62} \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & -2\pi_{62} \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & \pi_{45} & 0 \\ 0 & 0 & 0 & -\pi_{45} & \pi_{44} & 0 \\ -\pi_{62} & \pi_{62} & 0 & 0 & 0 & \pi_{66} \end{matrix}$	23, $m3$ 4 comp.	$\begin{matrix} p_{11} & p_{12} & p_{21} & 0 & 0 & 0 \\ p_{21} & p_{11} & p_{12} & 0 & 0 & 0 \\ p_{12} & p_{21} & p_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & p_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & p_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & p_{44} \end{matrix}$
4, $\bar{4}$, $4/m$ 10 comp., 9 inv.	$\begin{matrix} p_{11} & p_{12} & p_{13} & 0 & 0 & p_{16} \\ p_{12} & p_{11} & p_{13} & 0 & 0 & -p_{16} \\ p_{31} & p_{31} & p_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & p_{44} & p_{45} & 0 \\ 0 & 0 & 0 & -p_{45} & p_{44} & 0 \\ p_{61} & -p_{61} & 0 & 0 & 0 & p_{66} \end{matrix}$	432, $\bar{4}3m$, $m3m$ 3 comp. $\infty\infty$, $\infty\infty m$ 2 comp. **)	$\begin{matrix} p_{11} & p_{12} & p_{12} & 0 & 0 & 0 \\ p_{12} & p_{11} & p_{12} & 0 & 0 & 0 \\ p_{12} & p_{12} & p_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & p_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & p_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & p_{44} \end{matrix}$

*) In classes 3, $\bar{3}$, 32, $3m$, $\bar{3}m$, 6, $\bar{6}$, $6/m$, 622, $6mm$, $6/mmm$, ∞, ∞/m, $\infty 2$, ∞m, ∞/mm $p_{66} = \frac{1}{2}(p_{11} - p_{12})$, $\pi_{66} = \pi_{11} - \pi_{22}$.

**) In classes $\infty\infty$ and $\infty\infty m$ $p_{44} = \frac{1}{2}(p_{11} - p_{12})$, $\pi_{44} = \pi_{11} - \pi_{12}$.

Table E.20

$[(V^2)]^2$ — Fourth-Rank Tensor n Symmetric with Respect to the Permutation of the Pairs of Indices:

$$n_{klij} = n_{ijkl}$$

Classes	n_{ijkl}								
1, $\bar{1}$ 45 comp., 42 inv.	n_{1111}	n_{1122}	n_{1133}	n_{1123}	n_{1131}	n_{1112}	n_{1132}	n_{1113}	n_{1121}
		n_{2222}	n_{2233}	n_{2223}	n_{2231}	n_{2212}	n_{2232}	n_{2213}	n_{2221}
			n_{3333}	n_{3323}	n_{3331}	n_{3312}	n_{3332}	n_{3313}	n_{3321}
				n_{2323}	n_{2331}	n_{2312}	n_{2332}	n_{2313}	n_{2321}
					n_{3131}	n_{3112}	n_{3132}	n_{3113}	n_{3121}
						n_{1212}	n_{1232}	n_{1213}	n_{1221}
							n_{3232}	n_{3213}	n_{3221}
								n_{1313}	n_{1321}
									n_{2121}

Table E.20 (cont'd)

Classes	n_{ijkl}								
2, m, $2/m$ ($2 \parallel X_2$, $m \perp X_2$) 25 comp., 24 inv.	n_{1111}	n_{1122}	n_{1133}	0	n_{1131}	0	0	n_{1113}	0
		n_{2222}	n_{2233}	0	n_{2231}	0	0	n_{2213}	0
			n_{3333}	0	n_{3331}	0	0	n_{3313}	0
				n_{2323}	0	n_{2312}	n_{2332}	0	n_{2321}
					n_{3131}	0	0	n_{3113}	0
						n_{1212}	n_{1232}	0	n_{1221}
							n_{3232}	0	n_{3221}
								n_{1313}	0
									n_{2121}
2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$) 25 comp., 24 inv.	n_{1111}	n_{1122}	n_{1133}	0	0	n_{1112}	0	0	n_{1121}
		n_{2222}	n_{2233}	0	0	n_{2212}	0	0	n_{2221}
			n_{3333}	0	0	n_{3312}	0	0	n_{3321}
				n_{2323}	n_{2331}	0	n_{2332}	n_{2313}	0
					n_{3131}	0	n_{3132}	n_{3113}	0
						n_{1212}	0	0	n_{1221}
							n_{3232}	n_{3213}	0
								n_{1313}	0
									n_{2121}
222, $mm2$, mmm 15 comp.	n_{1111}	n_{1122}	n_{1133}	0	0	0	0	0	0
		n_{2222}	n_{2233}	0	0	0	0	0	0
			n_{3333}	0	0	0	0	0	0
				n_{2323}	0	0	n_{2332}	0	0
					n_{3131}	0	0	n_{3113}	0
						n_{1212}	0	0	n_{1221}
							n_{3232}	0	0
								n_{1313}	0
									n_{2121}
4, $\bar{4}$, $4/m$ 13 comp., 12 inv.	n_{1111}	n_{1122}	n_{1133}	0	0	n_{1112}	0	0	$-n_{2212}$
		n_{1111}	n_{1133}	0	0	n_{2212}	0	0	$-n_{1112}$
			n_{3333}	0	0	n_{3312}	0	0	$-n_{3312}$
				n_{2323}	n_{2331}	0	n_{2332}	0	0
					n_{3131}	0	0	n_{2332}	0
						n_{1212}	0	0	n_{1221}
							n_{3131}	$-n_{2331}$	0
								n_{2323}	0
									n_{1212}
422, $4mm$, $\bar{4}2m$, $4/mmm$ 9 comp.	n_{1111}	n_{1122}	n_{1133}	0	0	0	0	0	0
		n_{1111}	n_{1133}	0	0	0	0	0	0
			n_{3333}	0	0	0	0	0	0
				n_{2323}	0	0	n_{2332}	0	0
					n_{3131}	0	0	n_{3113}	0
						n_{1212}	0	0	n_{1221}
							n_{3131}	0	0
								n_{2323}	0
									n_{1212}

Table E.20 (cont'd)

Classes	n_{ijkl}								
3, $\bar{3}$ 15 comp., 14 inv. *)	n_{1111}	n_{1122}	n_{1133}	n_{1123}	n_{1131}	n_{1112}	n_{1132}	n_{1113}	$-n_{1112}$
		n_{1111}	n_{1133}	$-n_{1123}$	$-n_{1131}$	n_{1112}	$-n_{1132}$	$-n_{1113}$	$-n_{1112}$
			n_{3333}	0	0	n_{3312}	0	0	$-n_{3312}$
				n_{2323}	n_{2331}	$-n_{1113}$	n_{2332}	0	$-n_{1113}$
					n_{3131}	n_{1132}	0	n_{2332}	n_{1132}
						n_{1212}	$-n_{1131}$	n_{1123}	n_{1221}
							n_{3131}	$-n_{2331}$	$-n_{1131}$
								n_{2323}	n_{1123}
									n_{1212}
32, 3m, $\bar{3}m$ 10 comp.*)	n_{1111}	n_{1122}	n_{1133}	n_{1123}	0	0	n_{1132}	0	0
		n_{1111}	n_{1133}	$-n_{1123}$	0	0	$-n_{1132}$	0	0
			n_{3333}	0	0	0	0	0	0
				n_{2323}	0	0	n_{2332}	0	0
					n_{3131}	n_{1132}	0	n_{2332}	n_{1132}
						n_{1212}	0	n_{1123}	n_{1221}
							n_{3131}	0	0
								n_{2323}	n_{1123}
									n_{1212}
6, $\bar{6}$ $6/m$, ∞, ∞/m 11 comp.*)	n_{1111}	n_{1122}	n_{1133}	0	0	n_{1112}	0	0	$-n_{1112}$
		n_{1111}	n_{1133}	0	0	n_{1112}	0	0	$-n_{1112}$
			n_{3333}	0	0	n_{3312}	0	0	$-n_{3312}$
				n_{2323}	n_{2331}	0	n_{2332}	0	0
					n_{3131}	0	0	n_{2332}	0
						n_{1212}	0	0	n_{1221}
							n_{3131}	$-n_{2331}$	0
								n_{2323}	0
									n_{1212}
622, $6mm$, $\bar{6}m2$, $6/mmm$, $\infty 2$, ∞m, ∞/mm 8 comp.*)	n_{1111}	n_{1122}	n_{1133}	0	0	0	0	0	0
		n_{1111}	n_{1133}	0	0	0	0	0	0
			n_{3333}	0	0	0	0	0	0
				n_{2323}	0	0	n_{2332}	0	0
					n_{3131}	0	0	n_{2332}	0
						n_{1212}	0	0	n_{1221}
							n_{3131}	0	0
								n_{2323}	0
									n_{1212}
23, $m3$ 5 comp.	n_{1111}	n_{1122}	n_{1122}	0	0	0	0	0	0
		n_{1111}	n_{1122}	0	0	0	0	0	0
			n_{1111}	0	0	0	0	0	0
				n_{2323}	0	0	n_{2332}	0	0
					n_{2323}	0	0	n_{2332}	0
						n_{2323}	0	0	n_{2332}
							n_{3232}	0	0
								n_{3232}	0
									n_{3232}

Table E.20 (cont'd)

Classes	n_{ijkl}								
432, $\bar{4}3m$, $m3m$ 4 comp. $\infty\infty$, $\infty\infty m$ 3 comp. **)	n_{1111}	n_{1122}	n_{1122}	0	0	0	0	0	0
		n_{1111}	n_{1122}	0	0	0	0	0	0
			n_{1111}	0	0	0	0	0	0
				n_{2323}	0	0	n_{2332}	0	0
					n_{2323}	0	0	n_{2332}	0
						n_{2323}	0	0	n_{2332}
							n_{2323}	0	0
								n_{2323}	0
									n_{2323}

*) In classes 3, $\bar{3}$, 32, $3m$, $\bar{3}m$, 6, $\bar{6}$, $6/m$, 622, $6mm$, $\bar{6}m2$, $6/mmm$, ∞, ∞/m, $\infty 2$, ∞m, ∞/mm $n_{1111} = n_{1122} + n_{1212} + n_{1221}$.

**) In classes $\infty\infty$ and $\infty\infty m$ $n_{1111} = n_{1122} + n_{2323} + n_{2332}$

Table E.21

[V^2] V^2—Fourth-Rank Tensor h Symmetric with Respect to Two Indices: $h_{jikl} = h_{ijkl}$

Classes	h_{ijkl}								
1, $\bar{1}$ 54 comp., 51 inv.	h_{1111}	h_{1122}	h_{1133}	h_{1123}	h_{1131}	h_{1112}	h_{1132}	h_{1113}	h_{1121}
	h_{2211}	h_{2222}	h_{2233}	h_{2223}	h_{2231}	h_{2212}	h_{2232}	h_{2213}	h_{2221}
	h_{3311}	h_{3322}	h_{3333}	h_{3323}	h_{3331}	h_{3312}	h_{3332}	h_{3313}	h_{3321}
	h_{2311}	h_{2322}	h_{2333}	h_{2323}	h_{2331}	h_{2312}	h_{2332}	h_{2313}	h_{2321}
	h_{3111}	h_{3122}	h_{3133}	h_{3123}	h_{3131}	h_{3112}	h_{3132}	h_{3113}	h_{3121}
	h_{1211}	h_{1222}	h_{1233}	h_{1223}	h_{1231}	h_{1212}	h_{1232}	h_{1213}	h_{1221}
2, m, $2/m$ ($2 \parallel X_2$, $m \perp X_2$) 28 comp., 27 inv.	h_{1111}	h_{1122}	h_{1133}	0	h_{1131}	0	0	h_{1113}	0
	h_{2211}	h_{2222}	h_{2233}	0	h_{2231}	0	0	h_{2213}	0
	h_{3311}	h_{3322}	h_{3333}	0	h_{3331}	0	0	h_{3313}	0
	0	0	0	h_{2323}	0	h_{2312}	h_{2332}	0	h_{2321}
	h_{3111}	h_{3122}	h_{3133}	0	h_{3131}	0	0	h_{3113}	0
	0	0	0	h_{1223}	0	h_{1212}	h_{1232}	0	h_{1221}
2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$) 28 comp., 27 inv.	h_{1111}	h_{1122}	h_{1133}	0	0	h_{1112}	0	0	h_{1121}
	h_{2211}	h_{2222}	h_{2233}	0	0	h_{2212}	0	0	h_{2221}
	h_{3311}	h_{3322}	h_{3333}	0	0	h_{3312}	0	0	h_{3321}
	0	0	0	h_{2323}	h_{2331}	0	h_{2332}	h_{2313}	0
	0	0	0	h_{3123}	h_{3131}	0	h_{3132}	h_{3113}	0
	h_{1211}	h_{1222}	h_{1233}	0	0	h_{1212}	0	0	h_{1221}

Table E.21 (cont'd)

Classes	h_{ijkl}								
222, $mm2$, mmm, 15 comp.	h_{1111}	h_{1122}	h_{1133}	0	0	0	0	0	0
	h_{2211}	h_{2222}	h_{2233}	0	0	0	0	0	0
	h_{3311}	h_{3322}	h_{3333}	0	0	0	0	0	0
	0	0	0	h_{2323}	0	0	h_{2332}	0	0
	0	0	0	0	h_{3131}	0	0	h_{3113}	0
	0	0	0	0	0	h_{1212}	0	0	h_{1221}
4, $\bar{4}$, $4/m$ 14 comp., 13 inv.	h_{1111}	h_{1122}	h_{1133}	0	0	h_{1112}	0	0	$-h_{2212}$
	h_{1122}	h_{1111}	h_{1133}	0	0	h_{2212}	0	0	$-h_{1112}$
	h_{3311}	h_{3311}	h_{3333}	0	0	h_{3312}	0	0	$-h_{3312}$
	0	0	0	h_{2323}	h_{2331}	0	h_{3131}	$-h_{3123}$	0
	0	0	0	h_{3123}	h_{3131}	0	$-h_{2331}$	h_{2323}	0
	h_{1211}	$-h_{1211}$	0	0	0	h_{1212}	0	0	h_{1212}
422, $4mm$, $\bar{4}2m$, $4/mmm$ 8 comp.	h_{1111}	h_{1122}	h_{1133}	0	0	0	0	0	0
	h_{1122}	h_{1111}	h_{1133}	0	0	0	0	0	0
	h_{3311}	h_{3311}	h_{3333}	0	0	0	0	0	0
	0	0	0	h_{2323}	0	0	h_{3131}	0	0
	0	0	0	0	h_{3131}	0	0	h_{2323}	0
	0	0	0	0	0	h_{1212}	0	0	h_{1212}
3, $\bar{3}$ 18 comp., 17 inv. *)	h_{1111}	h_{1122}	h_{1133}	h_{1123}	h_{1131}	h_{1112}	h_{1132}	h_{1113}	$-h_{2212}$
	h_{1122}	h_{1111}	h_{1133}	$-h_{1123}$	$-h_{1131}$	h_{2212}	$-h_{1132}$	$-h_{1113}$	$-h_{1112}$
	h_{3311}	h_{3311}	h_{3333}	0	0	h_{3312}	0	0	$-h_{3312}$
	h_{2311}	$-h_{2311}$	0	h_{2323}	h_{2331}	$-h_{3111}$	h_{3131}	$-h_{3123}$	$-h_{3111}$
	h_{3111}	$-h_{3111}$	0	h_{3123}	h_{3131}	h_{2311}	$-h_{2331}$	h_{2323}	h_{2311}
	h_{1211}	$-h_{1211}$	0	$-h_{1113}$	h_{1132}	h_{1212}	$-h_{1131}$	h_{1123}	h_{1212}
32, $3m$, $\bar{3}m$ 10 comp.**)	h_{1111}	h_{1122}	h_{1133}	h_{1123}	0	0	h_{1132}	0	0
	h_{1122}	h_{1111}	h_{1133}	$-h_{1123}$	0	0	$-h_{1132}$	0	0
	h_{3311}	h_{3311}	h_{3333}	0	0	0	0	0	0
	h_{2311}	$-h_{2311}$	0	h_{2323}	0	0	h_{3131}	0	0
	0	0	0	0	h_{3131}	h_{2311}	0	h_{2323}	h_{2311}
	0	0	0	0	h_{1132}	h_{1212}	0	h_{1123}	h_{1212}
6, $\bar{6}$, $6/m$, ∞ ∞/m 12 comp.*)	h_{1111}	h_{1122}	h_{1133}	0	0	h_{1112}	0	0	$-h_{2212}$
	h_{1122}	h_{1111}	h_{1133}	0	0	h_{2212}	0	0	$-h_{1112}$
	h_{3311}	h_{3311}	h_{3333}	0	0	h_{3312}	0	0	$-h_{3312}$
	0	0	0	h_{2323}	h_{2331}	0	h_{3131}	$-h_{3123}$	0
	0	0	0	h_{3123}	h_{3131}	0	$-h_{2331}$	h_{2323}	0
	h_{1211}	$-h_{1211}$	0	0	0	h_{1212}	0	0	h_{1212}
622, $6mm$, $\bar{6}m2$, $6/mmm$, $\infty 2$, ∞m ∞/mm 7 comp.**)	h_{1111}	h_{1122}	h_{1133}	0	0	0	0	0	0
	h_{1122}	h_{1111}	h_{1133}	0	0	0	0	0	0
	h_{3311}	h_{3311}	h_{3333}	0	0	0	0	0	0
	0	0	0	h_{2323}	0	0	h_{3131}	0	0
	0	0	0	0	h_{3131}	0	0	h_{2323}	0
	0	0	0	0	0	h_{1212}	0	0	h_{1212}

Table E.21 (cont'd)

Classes	h_{ijkl}								
23, $m3$ 5 comp.	h_{1111}	h_{1122}	h_{2211}	0	0	0	0	0	0
	h_{2211}	h_{1111}	h_{1122}	0	0	0	0	0	0
	h_{1122}	h_{2211}	h_{1111}	0	0	0	0	0	0
	0	0	0	h_{2323}	0	0	h_{2332}	0	0
	0	0	0	0	h_{2323}	0	0	h_{2332}	0
	0	0	0	0	0	h_{2323}	0	0	h_{2332}
432, $43m$, $m3m$ 3 comp. $\infty\infty\infty$, $\infty\infty m$ 2 comp.***)	h_{1111}	h_{1122}	h_{1122}	0	0	0	0	0	0
	h_{1122}	h_{1111}	h_{1122}	0	0	0	0	0	0
	h_{1122}	h_{1122}	h_{1111}	0	0	0	0	0	0
	0	0	0	h_{2323}	0	0	h_{2323}	0	0
	0	0	0	0	h_{2323}	0	0	h_{2323}	0
	0	0	0	0	0	h_{2323}	0	0	h_{2323}

*) In classes 3, $\bar{3}$, 6, $\bar{6}$, $6/m$, ∞, ∞/m $h_{1111} = h_{1122} + 2h_{1212}$ and $h_{2212} - h_{1112} = 2h_{1211}$.
**) In classes 32, $3m$, $\bar{3}m$, 622, $6mm$, $\bar{6}m2$, $6/mmm$, $\infty 2$, ∞m, ∞/mm $h_{1111} = h_{1122} + 2h_{1212}$.
***) In classes $\infty\infty\infty$ and $\infty\infty m$ $h_{1111} = h_{1122} + 2h_{2323}$.

Table E.22

V — Fourth-Rank Tensor b

Classes	b_{ijkl}								
1, $\bar{1}$ 81 comp., 78 inv.	b_{1111}	b_{1122}	b_{1133}	b_{1123}	b_{1131}	b_{1112}	b_{1132}	b_{1113}	b_{1121}
	b_{2211}	b_{2222}	b_{2233}	b_{2223}	b_{2231}	b_{2212}	b_{2232}	b_{2213}	b_{2221}
	b_{3311}	b_{3322}	b_{3333}	b_{3323}	b_{3331}	b_{3312}	b_{3332}	b_{3313}	b_{3321}
	b_{2311}	b_{2322}	b_{2333}	b_{2323}	b_{2331}	b_{2312}	b_{2332}	b_{2313}	b_{2321}
	b_{3111}	b_{3122}	b_{3133}	b_{3123}	b_{3131}	b_{3112}	b_{3132}	b_{3113}	b_{3121}
	b_{1211}	b_{1222}	b_{1233}	b_{1223}	b_{1231}	b_{1212}	b_{1232}	b_{1213}	b_{1221}
	b_{3211}	b_{3222}	b_{3233}	b_{3223}	b_{3231}	b_{3212}	b_{3232}	b_{3213}	b_{3221}
	b_{1311}	b_{1322}	b_{1333}	b_{1323}	b_{1331}	b_{1312}	b_{1332}	b_{1313}	b_{1321}
	b_{2111}	b_{2122}	b_{2133}	b_{2123}	b_{2131}	b_{2112}	b_{2132}	b_{2113}	b_{2121}
2, m, $2/m$ ($2 \parallel X_2$, $m \perp X_2$) 41 comp., 40 inv.	b_{1111}	b_{1122}	b_{1133}	0	b_{1131}	0	0	b_{1113}	0
	b_{2211}	b_{2222}	b_{2233}	0	b_{2231}	0	0	b_{2213}	0
	b_{3311}	b_{3322}	b_{3333}	0	b_{3331}	0	0	b_{3313}	0
	0	0	0	b_{2323}	0	b_{2312}	b_{2332}	0	b_{2321}
	b_{3111}	b_{3122}	b_{3133}	0	b_{3131}	0	0	b_{3113}	0
	0	0	0	b_{1223}	0	b_{1212}	b_{1232}	0	b_{1221}
	0	0	0	b_{3223}	0	b_{3212}	b_{3232}	0	b_{3221}
	b_{1311}	b_{1322}	b_{1333}	0	b_{1331}	0	0	b_{1313}	0
	0	0	0	b_{2123}	0	b_{211}	b_{2132}	0	b_{2121}

Table E.22 (cont'd)

Classes	b_{ijkl}								
2, m, $2/m$ ($2 \parallel X_3$, $m \perp X_3$) 41 comp., 40 inv.	b_{1111}	b_{1122}	b_{1133}	0	0	b_{1112}	0	0	b_{1121}
	b_{2211}	b_{2222}	b_{2233}	0	0	b_{2212}	0	0	b_{2221}
	b_{3311}	b_{3322}	b_{3333}	0	0	b_{3312}	0	0	b_{3321}
	0	0	0	b_{2323}	b_{2331}	0	b_{2332}	b_{2313}	0
	0	0	0	b_{3123}	b_{3131}	0	b_{3132}	b_{3113}	0
	b_{1211}	b_{1222}	b_{1233}	0	0	b_{1212}	0	0	b_{1221}
	0	0	0	b_{3223}	b_{3231}	0	b_{3232}	b_{3213}	0
	0	0	0	b_{1323}	b_{1331}	0	b_{1332}	b_{1313}	0
	b_{2111}	b_{2122}	b_{2133}	0	0	b_{2112}	0	0	b_{2121}
222, $mm2$, mmm 21 comp.	b_{1111}	b_{1122}	b_{1133}	0	0	0	0	0	0
	b_{2211}	b_{2222}	b_{2233}	0	0	0	0	0	0
	b_{3311}	b_{3322}	b_{3333}	0	0	0	0	0	0
	0	0	0	b_{2323}	0	0	b_{2332}	0	0
	0	0	0	0	b_{3131}	0	0	b_{3113}	0
	0	0	0	0	0	b_{1212}	0	0	b_{1221}
	0	0	0	b_{3223}	0	0	b_{3232}	0	0
	0	0	0	0	b_{1331}	0	0	b_{1313}	0
	0	0	0	0	0	b_{2112}	0	0	b_{2121}
4, $\bar{4}$, $4/m$ 21 comp., 20 inv.	b_{1111}	b_{1122}	b_{1133}	0	0	b_{1112}	0	0	$-b_{2212}$
	b_{1122}	b_{1111}	b_{1133}	0	0	b_{2212}	0	0	$-b_{1112}$
	b_{3311}	b_{3311}	b_{3333}	0	0	b_{3312}	0	0	$-b_{3312}$
	0	0	0	b_{2323}	b_{2331}	0	b_{2332}	b_{2313}	0
	0	0	0	b_{3123}	b_{3131}	0	b_{3132}	b_{3113}	0
	b_{1211}	b_{1222}	b_{1233}	0	0	b_{1212}	0	0	b_{1221}
	0	0	0	b_{3113}	$-b_{3132}$	0	b_{3131}	$-b_{3123}$	0
	0	0	0	$-b_{2313}$	b_{2332}	0	$-b_{2331}$	b_{2323}	0
	$-b_{1222}$	$-b_{1211}$	$-b_{1233}$	0	0	b_{1221}	0	0	b_{1212}
422, $4mm$, $42m$, $4/mmm$ 11 comp.	b_{1111}	b_{1122}	b_{1133}	0	0	0	0	0	0
	b_{1122}	b_{1111}	b_{1133}	0	0	0	0	0	0
	b_{3311}	b_{3311}	b_{3333}	0	0	0	0	0	0
	0	0	0	b_{2323}	0	0	b_{2332}	0	0
	0	0	0	0	b_{3131}	0	0	b_{3113}	0
	0	0	0	0	0	b_{1212}	0	0	b_{1221}
	0	0	0	b_{3113}	0	0	b_{3131}	0	0
	0	0	0	0	b_{2332}	0	0	b_{2323}	0
	0	0	0	0	0	b_{1221}	0	0	b_{1212}
3, $\bar{3}$ 27 comp., 26 inv. *)	b_{1111}	b_{1122}	b_{1133}	b_{1123}	b_{1131}	b_{1112}	b_{1132}	b_{1113}	$-b_{2212}$
	b_{1122}	b_{1111}	b_{1133}	$-b_{1123}$	$-b_{1131}$	b_{2212}	$-b_{1132}$	$-b_{1113}$	$-b_{1112}$
	b_{3311}	b_{3311}	b_{3333}	0	0	b_{3312}	0	0	$-b_{3312}$
	b_{2311}	$-b_{2311}$	0	b_{2323}	b_{2331}	$-b_{1311}$	b_{2332}	b_{2313}	$-b_{1311}$
	b_{3111}	$-b_{3111}$	0	b_{3123}	b_{3131}	b_{3211}	b_{3132}	b_{3113}	b_{3211}
	b_{1211}	b_{1222}	b_{1233}	$-b_{1113}$	b_{1132}	b_{1212}	$-b_{1131}$	b_{1123}	b_{1221}
	b_{3211}	$-b_{3211}$	0	b_{3113}	$-b_{3132}$	$-b_{3111}$	b_{3131}	$-b_{3123}$	$-b_{3111}$
	b_{1311}	$-b_{1311}$	0	$-b_{2313}$	b_{2332}	b_{2311}	$-b_{2331}$	b_{2323}	b_{2311}
	$-b_{1222}$	$-b_{1211}$	$-b_{1233}$	$-b_{1113}$	b_{1132}	b_{1221}	$-b_{1131}$	b_{1123}	b_{1212}

Table E.22 *(cont'd)*

Classes	b_{ijkl}								
32, $3m$, $\bar{3}m$ 11 comp. **)	b_{1111}	b_{1122}	b_{1133}	b_{1123}	0	0	b_{1132}	0	0
	b_{1122}	b_{1111}	b_{1133}	$-b_{1123}$	0	0	$-b_{1132}$	0	0
	b_{3311}	b_{3311}	b_{3333}	0	0	0	0	0	0
	b_{2311}	$-b_{2311}$	0	b_{2323}	0	0	b_{2332}	0	0
	0	0	0	0	b_{3131}	b_{3211}	0	b_{3113}	b_{3211}
	0	0	0	0	b_{1132}	b_{1212}	0	b_{1123}	b_{1221}
	b_{3211}	$-b_{3211}$	0	b_{3113}	0	0	b_{3131}	0	0
	0	0	0	0	b_{2332}	b_{2311}	0	b_{2323}	b_{2311}
	0	0	0	0	b_{1132}	b_{1221}	0	b_{1123}	b_{1212}
6, $\bar{6}$, $6/m$, ∞, ∞/m 19 comp.*)	b_{1111}	b_{1122}	b_{1133}	0	0	b_{1112}	0	0	$-b_{2212}$
	b_{1122}	b_{1111}	b_{1133}	0	0	b_{2212}	0	0	$-b_{1112}$
	b_{3311}	b_{3311}	b_{3333}	0	0	b_{3312}	0	0	$-b_{3312}$
	0	0	0	b_{2323}	b_{2331}	0	b_{2332}	b_{2313}	0
	0	0	0	b_{3123}	b_{3131}	0	b_{3132}	b_{3113}	0
	b_{1211}	b_{1222}	b_{1233}	0	0	b_{1212}	0	0	b_{1221}
	0	0	0	b_{3113}	$-b_{3132}$	0	b_{3131}	$-b_{3123}$	0
	0	0	0	$-b_{2313}$	b_{2332}	0	$-b_{2331}$	b_{2323}	0
	$-b_{1222}$	$-b_{1211}$	$-b_{1233}$	0	0	b_{1221}	0	0	b_{1212}
622, $6mm$, $\bar{6}m2$, $6/mmm$, $\infty 2$, ∞m, ∞/mm 10 comp. **)	b_{1111}	b_{1122}	b_{1133}	0	0	0	0	0	0
	b_{1122}	b_{1111}	b_{1133}	0	0	0	0	0	0
	b_{3311}	b_{3311}	b_{3333}	0	0	0	0	0	0
	0	0	0	b_{2323}	0	0	b_{2332}	0	0
	0	0	0	0	b_{3131}	0	0	b_{3113}	0
	0	0	0	0	0	b_{1212}	0	0	b_{1221}
	0	0	0	b_{3113}	0	0	b_{3131}	0	0
	0	0	0	0	b_{2332}	0	0	b_{2323}	0
	0	0	0	0	0	b_{1221}	0	0	b_{1212}
23, $m3$ 7 comp.	b_{1111}	b_{1122}	b_{2211}	0	0	0	0	0	0
	b_{2211}	b_{1111}	b_{1122}	0	0	0	0	0	0
	b_{1122}	b_{2211}	b_{1111}	0	0	0	0	0	0
	0	0	0	b_{2323}	0	0	b_{2332}	0	0
	0	0	0	0	b_{2323}	0	0	b_{2332}	0
	0	0	0	0	0	b_{2323}	0	0	b_{2332}
	0	0	0	b_{3223}	0	0	b_{3232}	0	0
	0	0	0	0	b_{3223}	0	0	b_{3232}	0
	0	0	0	0	0	b_{3223}	0	0	b_{3232}

Table E.22 (cont'd)

Classes	b_{ijkl}								
432, $43m$, $m3m$ 4 comp. $\infty\infty\infty$, $\infty\infty\infty m$ 3 comp. **)	b_{1111}	b_{1122}	b_{1122}	0	0	0	0	0	0
	b_{1122}	b_{1111}	b_{1122}	0	0	0	0	0	0
	b_{1122}	b_{1122}	b_{1111}	0	0	0	0	0	0
	0	0	0	b_{2323}	0	0	b_{2332}	0	0
	0	0	0	0	b_{2323}	0	0	b_{2332}	0
	0	0	0	0	0	b_{2323}	0	0	b_{2332}
	0	0	0	b_{2332}	0	0	b_{2323}	0	0
	0	0	0	0	b_{2332}	0	0	b_{2323}	0
	0	0	0	0	0	b_{2332}	0	0	b_{2323}

*) In classes 3, 3, 6, $\bar{6}$, $6/m$, ∞, ∞/m $b_{1111} = b_{1122} + b_{1212} + b_{1221}$ and $b_{1112} - b_{2212} = b_{1222} - b_{1211}$.
**) In classes 32, $3m$, $\bar{3}m$, 622, $6mm$, $\bar{6}m2$, $6/mmm$, $\infty 2$, ∞m and ∞/mm $b_{1111} = b_{1122} + b_{1212} + b_{1221}$.
***) In classes $\infty\infty$ and $\infty\infty m$ $b_{1111} = b_{1122} + b_{2323} + b_{2332}$.

Table E.23

$V[[V^2]^2]$ – Fifth-Rank Tensor Q Symmetric with Respect to Two Pairs of Indices and to Their Permutation:

$$Q_{mijkl} = Q_{mjikl} = Q_{mijlk} = Q_{mklij}$$

for Several Crystallographic Classes

For other classes see Koptsik (1966). Below are given the coefficients $Q_{m\lambda\mu}$ related to the components Q_{mijkl} by recalculation rules

$$Q_{m\lambda\mu} = \begin{cases} Q_{mijkl} & (ij \leftrightarrow \lambda = 1, 2, 3; \quad kl \leftrightarrow \mu = 1, 2, 3), \\ 2Q_{mijkl} & (ij \leftrightarrow \lambda = 1, 2, 3; \quad kl \leftrightarrow \mu = 4, 5, 6), \\ 2Q_{mijkl} & (ij \leftrightarrow \lambda = 4, 5, 6; \quad kl \leftrightarrow \mu = 1, 2, 3), \\ 4Q_{mijkl} & (ij \leftrightarrow \lambda = 4, 5, 6; \quad kl \leftrightarrow \mu = 4, 5, 6). \end{cases}$$

Indices are given only for non-zero coefficients; expressions of the form $216 = 111 + 3 \cdot 122$ mean $Q_{216} = Q_{111} + 3Q_{122}$.

Class 222 (12 comp.): 114, 124, 134, 156, 215, 225, 235, 246, 316, 326, 336, 345.

Class 32 (8 comp.): $166 = 2 \cdot 112 = -2(111 + 122)$, $216 = 111 + 3 \cdot 122$, $226 = -3 \cdot 111 - 122$, $236 = 2 \cdot 123 = -2 \cdot 113$, $225 = -114$, $215 = -124$, $246 = -156 = 114 - 124$, $235 = -134$, $245 = 2 \cdot 144 = -2 \cdot 155$, $346 = 2 \cdot 325 = -2 \cdot 315$.

Class $42m$ (7 comp.): $114 = 225$, $124 = 215$, $134 = 235$, $156 = 246$, $316 = 326$, 336, 345.

Class $43m$ (3 comp.): $114 = 225 = 336$, $124 = 235 = 316 = 134 = 215 = 326$, $156 = 246 = 345$.

Class 432 (1 comp.): $124 = 235 = 316 = -134 = -215 = -326$.

Table E.24

$[[[V^2]]^3]$ — Sixth-Rank Tensor C Symmetric with Respect to the First, Second, Third Pairs of Indices and to Their Permutations for Several Crystallographic and Limit Classes:

$$C_{ijklmn} = C_{jiklmn} = C_{ijlkmn} = C_{ijklnm} = C_{ijmnkl} = C_{klijmn}$$

For other classes see Mason (1966) or Fumi (1951, 1952b).

Below are given coefficients $C_{\lambda\mu\nu}$ connected with tensor components C_{ijklmn} by the recalculation rules

$$C_{\lambda\mu\nu} = C_{ijklmn} \quad (ij \leftrightarrow \lambda, \quad kl \leftrightarrow \mu, \quad mn \leftrightarrow \nu, \ \lambda, \ \mu, \ \nu = 1, \ldots, 6)$$

Indices are given only for non-zero coefficients (see explanation for Table E.23).

Classes 222, $mm2$, mmm (20 comp.): 111, 112, 113, 122, 123, 133, 144, 155, 166, 222, 223, 233, 244, 255, 266, 333, 344, 355, 366, 456.

Classes 32, $3m$, $\bar{3}m$ (14 comp.): 111, 112, 113, 114, 122 = 111 + +112 — 222, 123, 124, 133, 134, 144, 155, 156 = 1/2 (114 + 3·124), 166 = —1/4 (2·111 + 112 — 3·222), 222, 223 = 113, 224 = —114 — — 2·124, 233 = 133, 234 = —134, 244 = 155, 255 = 144, 256 = = 1/2 (114 — 124), 266 = 1/4 (2·111 — 122 — 222), 333, 344 = 355, 356 = 134, 366 = 1/2 (113 — 123), 444 = —455, 456 = —1/2 (144 — — 155), 466 = 124.

Classes 422, $4mm$, $\bar{4}2m$, $4/mmm$ (12 comp.): the same coefficients as in classes 222, $mm2$, mmm, but connected by relations: 122 = 112, 222 = 111, 223 = 113, 233 = 133, 244 = 155, 255 = 144, 266 = 166, 344 = 355.

Classes 432, $\bar{4}3m$, $m3m$ (6 comp.): 111 = 222 = 333, 112 = 113 = = 122 = 133 = 223 = 233, 123, 144 = 255 = 366, 155 = 166 = 244 = = 266 = 344 = 355, 456.

Classes $\infty\infty$, $\infty\infty m$ (3 comp.): the same coefficients as in classes 432, $\bar{4}3m$, $m3m$ differ from zero, but they are connected by additional relations: 144 = 1/2 (122 — 123), 155 = 1/4 (111 — 112), 456 = 1/8 (111 — — 3·112 + 2·123).

Table E.25

$[V^2]\,[[V^2]^2]$ — Sixth-Rank Tensor q Symmetric with Respect to the First, Second, Third Pairs of Indices and to the Permutation of the Second and Third Pairs, for Some Crystallographic and Limit Classes:

$$q_{ijklmn} = q_{jiklmn} = q_{ijlkmn} = q_{ijklnm} = q_{ijmnkl}$$

For other classes see Vedam and Srinivasan (1967).

We give coefficients $q_{\lambda\mu\nu}$ connected with the components q_{ijklmn} by recalculation rules $q_{\lambda\mu\nu} = q_{ijklmn}$ $(ij \leftrightarrow \lambda, kl \leftrightarrow \mu, mn \leftrightarrow \nu, \lambda, \mu, \nu = 1, \ldots, 6)$. Indices are given only for non-zero components (see explanation to Table E.23)

Classes 222, $mm2$, mmm (39 comp.): 111, 112, 113, 122, 123, 133, 144, 155, 166, 211, 212, 213, 222, 223, 233, 244, 255, 266, 311, 312, 313, 322, 323, 333, 344, 355, 366, 414, 424, 434, 456, 515, 525, 535, 546, 616, 626, 636, 645.

Classes 32, $3m$, $\bar{3}m$ (26 comp.): 111, 112, 113, 114, 122 = 111 + + 211 — 222, 123, 124, 133, 134, 144, 155, 156 = 1/2 (114 + 124 + + 2·214), 166 = —1/4 (2·111 + 2·112 — 211 — 3·222), 211, 212 = = 111 + 112 — 222, 213 = 123, 214, 222, 223 — 113, 224 = —114 — — 124 — 214, 233 = 133, 234 = —134, 244 = 155, 255 = 144, 256 = =1/2 (114 — 124), 266 = 1/4 (2·111 — 2·112 + 211 — 222), 311, 312, 313, 314, 322 = 311, 323 = 313, 324 = —314, 333, 344 = 355, 356 = =314, 366 = 1/2 (311 — 312), 411, 412, 413, 414, 422 = —411 — —2·412, 423 = —413, 424, 434, 444 = —455, 456 = 1/2 (424 — 414), 466 = 412, 515 = 424, 516 = 1/2 (411 + 3·412), 525 = 414, 526 = =1/2 (411 — 412), 535 = 434, 536 = 413, 545 = —444, 546 = = 1/2 424 — 414), 615 = 1/2 (114 + 2·124 + 214), 616 = —1/4 (2 × × 111 +211 — 3·222), 625 = 1/2 (114 — 214), 626 = 1/4 (2·111 — — 211 — 222), 635 = 134, 636 = 1/2 (113 — 123), 645 = —1/2 (144 — — 155), 646 = 1/2 (124 + 214).

Classes 422, $4mm$, $42m$, $4/mmm$ (22 comp.): the same coefficients as in classes 222, $mm2$, mmm, but connected by relations 211 = 122, 212 = = 112, 213 = 123, 222 = 111, 223 = 113, 233 = 133, 244 = 155, 255 = = 144, 266 = 166, 322 = 311, 323 = 313, 344 = 355, 515 = 424, 525 = 414, 535 = 434, 546 = 456, 616 = 626.

Classes 432, $\bar{4}3m$ $m3m$ (9 comp.): 111 = 222 = 333, 112 = 113 = = 212 = 223 = 313 = 323, 122 = 133 = 211 = 233 = 311 = 322, 123 = 213 = 312, 144 = 255 = 366, 155 = 166 = 244 = 266 = 344 = = 355, 414 = 525 = 636, 424 = 434 = 515 = 535 = 616 = 626, 456 = 546 = 645.

Classes $\infty\infty$, $\infty\infty m$ (4 comp.): the preceding equalities supplemented by relations 144 = 1/2 (122 — 123), 155 = 1/4 (111 — 2·112 + 122), 414 = 1/2 (112 — 123), 424 = 1/4 (111 — 122), 456 = 1/8 (111 — — 2·112 — 122 + 2·123).

F. CONTRACTED NOTATION OF TENSORS

In theoretical crystal physics one often has to deal with symmetric second rank tensors (internal symmetry $[V^2]$). Such are strain and stress tensors, as well as many matter tensors. The relations between such tensors are specified by different matter tensors of the fourth, sixth and still higher ranks having, for all their variety, one common property: they are all symmetric with respect to pairs of indices, i.e. they have internal symmetry $[V^2]^2$, $[V^2]^3$ and so forth. Although all calculations with these tensors can be done by the common methods of tensor algebra, it was found convenient to use special methods of calculation. These methods are based on the substitution of pairs of Latin indices i, j = = 1, 2, 3 by a single Greek index λ which can assume values from 1 to 6 (if indices i and j can be permuted, they form six different combinations). This is accompanied by halving the number of indices (the rank of the tensor is halved, so to say) true enough, this has to be paid for by an increased number of values taken by each index. The availability of supplementary internal symmetry of tensors, i.e. the possibility of interchanging individual pairs of indices, does

not prevent the use of this method; thus, it can also be used for tensors of types $[[V^2]^2]$, $[V^2]\,[[V^2]^2]$, $[[V^2]^3]$ and the like. Moreover, correspondingly modified, this method is also suitable for such tensors as $V\,[V^2]$, $V\,[[V^2]^2]$ and so forth.

We shall present this method by parts; each part is referred to a definite section of the main body of the book for the better perception of which it is required.

To Sec. 51. Tensors ε and σ. Let us replace the pair of indices ij by one index λ, according to the scheme

$$\begin{array}{llllll} ij = 11 & 22 & 33 & 23 & 31 & 12 \\ \lambda = 1 & 2 & 3 & 4 & 5 & 6 \end{array} \tag{F.1}$$

Further we shall assume that Greek indices λ, μ, ν, $\varkappa$ can have values, 1, ..., 6 and are connected with the pairs of Latin indices ij, kl and others by relations (F.1).

The transition from a pair of indices (say, ij) to one index (λ) for tensors ε and σ is performed differently. Quantities ε_λ are conventionally defined by the equalities

$$\begin{aligned} &\varepsilon_1 = \varepsilon_{11}, && \varepsilon_2 = \varepsilon_{22}, \\ &\varepsilon_3 = \varepsilon_{33}, && \varepsilon_4 = 2\varepsilon_{23}, \\ &\varepsilon_5 = 2\varepsilon_{31}, && \varepsilon_6 = 2\varepsilon_{12}; \end{aligned}$$

they are all combined into a formula

$$\varepsilon_\lambda = \begin{cases} \varepsilon_{ij} & (ij \longleftrightarrow \lambda = 1,\ 2,\ 3), \\ 2\varepsilon_{ij} & (ij \longleftrightarrow \lambda = 4,\ 5,\ 6). \end{cases} \tag{F.2}$$

The relations connecting ε_λ and ε_{ij} can also be expressed in the form

$$\varepsilon_{ij} = \frac{\varepsilon_\lambda}{2 - \delta_{ij}}. \tag{F.3}$$

We shall denote the corresponding quantities for the stress tensor σ^λ by a superscript, since they are defined by other relations, i.e.

$$\begin{aligned} &\sigma^1 = \sigma_{11}, && \sigma^2 = \sigma_{22}, \\ &\sigma^3 = \sigma_{33}, && \sigma^4 = \sigma_{23}, \\ &\sigma^5 = \sigma_{31}, && \sigma^6 = \sigma_{12}. \end{aligned}$$

These equalities are combined by the formula

$$\sigma^\lambda = \sigma_{ij} \qquad (ij \longleftrightarrow \lambda = 1,\ \ldots,\ 6). \tag{F.4}$$

Henceforth we shall denote by a subscript those quantities with one Greek index which are formed from the components of a second-rank tensor according to rule (F.2), and by a superscript those formed according to rule (F.4).

An important role in the theory of elasticity of crystals is played by the sum $\sigma_{ij}\varepsilon_{ij}$. The introduced notation permits writing it in the form

$$\sigma_{ij}\varepsilon_{ij} = \sigma^\lambda \varepsilon_\lambda, \tag{F.5}$$

where summation is meant to be done with respect to the repeating Greek indices written both as superscripts and subscripts. The difference between rules (F.2) and (F.4) is highly essential for the fulfilment of equality (F.5): if the quantities corresponding to the two tensors were formed by one and the same rule, whether (F.2) or (F.4), equality (F.5) could not be fulfilled. True enough, the transition to Greek indices for all symmetric second-rank tensors S could be done in the

same way, i.e.

$$S_\lambda = \begin{cases} S_{ij} & \text{at} \quad ij \leftrightarrow \lambda = 1,\ 2,\ 3, \\ \sqrt{2}\, S_{ij} & \text{at} \quad ij \leftrightarrow \lambda = 4,\ 5,\ 6. \end{cases} \tag{F.6}$$

In this case equality (F.5) would also be fulfilled and such a definition would be in many respects more convenient. But the transition from rules (F.2) and (F.4) to (F.6) would involve the recalculation of the tabulated values of the elastic and other coefficients and would hamper the use of the existing works, so we shall use the conventional method of notation in spite of its obvious disadvantage.

In the transition to a "new" system of coordinates constructed on the basis $e_{i'} = c_{i'k} e_k$, the components S_{kl} of any symmetric second-rank tensor S are transformed according to the law

$$S_{i'j'} \quad c_{i'k} c_{j'l} S_{kl}. \tag{F.7}$$

The quantities ε_μ and σ^μ also experience certain linear transformations:

$$\varepsilon_{\lambda'} = P^\mu_{\lambda'} \varepsilon_\mu, \tag{F.8}$$

$$\sigma^{\lambda'} = Q^{\lambda'}_\mu \sigma^\mu. \tag{F.9}$$

These transformations are written down so that the corresponding free indices are on the same level, and the summation is done with respect to indices located on different levels. The transformations must meet the requirement calling for quantities $\varepsilon_{\lambda'}$ and $\sigma^{\lambda'}$ in the new coordinate frame to be connected with the components of the corresponding tensors by the same rules (F.2) and (F.4) as in the old frame. Having extracted all the terms from (F.7) and replaced the components $S_{i'j'}$ and S_{kl} in one case by $\varepsilon_{\lambda'}$ and $\varepsilon_{\mu'}$, according to (F.2), and in another by $\sigma^{\lambda'}$ and σ^μ according to (F.4), we shall find the elements of matrices P and Q:

Matrix $P^\mu_{\lambda'}$

λ' \ μ	1	2	3	4	5	6
1′	$c^2_{1'1}$	$c^2_{1'2}$	$c^2_{1'3}$	$c_{1'2}c_{1'3}$	$c_{1'3}c_{1'1}$	$c_{1'1}c_{1'2}$
2′	$c^2_{2'1}$	$c^2_{2'2}$	$c^2_{2'3}$	$c_{2'2}c_{2'3}$	$c_{2'3}c_{2'1}$	$c_{2'1}c_{2'2}$
3′	$c^2_{3'1}$	$c^2_{3'2}$	$c^2_{3'3}$	$c_{3'2}c_{3'3}$	$c_{3'3}c_{3'1}$	$c_{3'1}c_{3'2}$
4′	$2c_{2'1}c_{3'1}$	$2c_{2'2}c_{3'2}$	$2c_{2'3}c_{3'3}$	$c_{2'2}c_{3'3} + c_{2'3}c_{3'2}$	$c_{2'3}c_{3'1} + c_{2'1}c_{3'3}$	$c_{2'1}c_{3'2} + c_{2'2}c_{3'1}$
5′	$2c_{3'1}c_{1'1}$	$2c_{3'2}c_{1'2}$	$2c_{3'3}c_{1'3}$	$c_{3'2}c_{1'3} + c_{3'3}c_{1'2}$	$c_{3'3}c_{1'1} + c_{3'1}c_{1'3}$	$c_{3'1}c_{1'2} + c_{3'2}c_{1'1}$
6′	$2c_{1'1}c_{2'1}$	$2c_{1'2}c_{2'2}$	$2c_{1'3}c_{2'3}$	$c_{1'2}c_{2'3} + c_{1'3}c_{2'2}$	$c_{1'3}c_{2'1} + c_{1'1}c_{2'3}$	$c_{1'1}c_{2'2} + c_{1'2}c_{2'1}$

Matrix $Q^{\mu}_{\lambda'}$

λ' \ μ	1	2	3	4	5	6
1′	$c_{1'1}$	$c^2_{1'2}$	$c^2_{1'3}$	$2c_{1'2}c_{1'3}$	$2c_{1'3}c_{1'1}$	$2c_{1'1}c_{1'2}$
2′	$c^2_{2'1}$	$c^2_{2'2}$	$c^2_{2'3}$	$2c_{2'2}c_{2'3}$	$2c_{2'3}c_{2'1}$	$2c_{2'1}c_{2'2}$
3′	$c^2_{3'1}$	$c^2_{3'2}$	$c^2_{3'3}$	$2c_{3'2}c_{3'3}$	$2c_{3'3}c_{3'1}$	$2c_{3'1}c_{3'2}$
4′	$c_{2'1}c_{3'1}$	$c_{2'2}c_{3'2}$	$c_{2'3}c_{3'3}$	$c_{2'2}c_{3'3}+$ $+c_{2'3}c_{3'2}$	$c_{2'3}c_{3'1}+$ $+c_{2'1}c_{3'3}$	$c_{2'1}c_{3'2}+$ $+c_{2'2}c_{3'1}$
5′	$c_{3'1}c_{1'1}$	$c_{3'2}c_{1'2}$	$c_{3'3}c_{1'3}$	$c_{3'2}c_{1'3}+$ $+c_{3'3}c_{1'2}$	$c_{3'3}c_{1'1}+$ $+c_{3'1}c_{1'3}$	$c_{3'1}c_{1'2}+$ $+c_{3'2}c_{1'1}$
6′	$c_{1'1}c_{2'1}$	$c_{1'2}c_{2'2}$	$c_{1'3}c_{2'3}$	$c_{1'2}c_{2'3}+$ $+c_{1'3}c_{2'2}$	$c_{1'3}c_{2'1}+$ $+c_{1'1}c_{2'3}$	$c_{1'1}c_{2'2}+$ $+c_{1'2}c_{2'1}$

The only difference between the matrices is this: in matrix Q the elements in the upper right-hand square contain coefficient 2, while in matrix P this coefficient is contained in the lower left-hand square. The elements of the matrices can be represented by means of the formulas

$$\frac{1}{2}(c_{i'k}c_{j'l}+c_{i'l}c_{j'k}) = \frac{P^{\mu}_{\lambda'}}{2-\delta_{i'j'}} = \frac{Q^{\lambda'}_{\mu}}{2-\delta_{kl}}, \tag{F.10}$$

where index λ' corresponds to the pair $i'j'$, and μ to the pair kl (see F.3).

In the transition from the new coordinate system to the old one, $\varepsilon_{\lambda'}$ and $\sigma^{\lambda'}$ experience, as can easily be verified, the following linear transformations:

$$\varepsilon_{\mu} = Q^{\lambda}_{\mu}\varepsilon_{\lambda'}, \tag{F.11}$$

$$\varepsilon^{\mu} = P^{\mu}_{\lambda'}\sigma^{\lambda'}. \tag{F.12}$$

The comparison of these formulas with (F.8) and (F.9) shows that the quantities of type ε_{μ} can be regarded as the covariant components of a certain vector in a six-dimensional space, while the quantities of type σ^{μ}, as the contravariant components of another vector in the same space. The difference between the transformation laws for these quantities—(F.8) and (F.11) for ε_{μ}, (F.9) and (F.12) for σ^{μ}—means that the basis to which they are referred is not orthonormalized (to an orthonormalized basis in a six-dimensional space there are referred quantities formed from the components of a symmetric second-rank tensor according to rule (F.6)).

To Sec. 51. Tensors c and s. According to Hooke's law, tensors σ and ε are connected by the linear relation

$$\sigma_{ij} = c_{ijkl}\varepsilon_{kl}, \tag{F.13}$$

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}, \tag{F.14}$$

where **c** and **s** are the fourth-rank tensors. Having replaced, according to scheme (F.1), the pairs of indices ij by index λ and kl by μ, we can write down

$$\sigma^{\lambda} = c^{\lambda\mu}\varepsilon_{\mu}, \tag{F.15}$$

$$\varepsilon_{\lambda} = s_{\lambda\mu}\sigma^{\mu}. \tag{F.16}$$

We wrote the indices of **c** and **s** according to rules formulated earlier. Upon the extraction of all terms from (F.13) and (F.15) and upon their comparison, we obtain the rule for the recalculation of $c^{\lambda\mu}$:

$$c^{\lambda\mu} = c_{ijkl} \quad (ij \leftrightarrow \lambda = 1, \ldots, 6; \quad kl \leftrightarrow \mu = 1, \ldots, 6). \tag{F.17}$$

Having done the same with equalities (F.14) and (F.16), we obtain the rule for $s_{\lambda\mu}$:

$$s_{\lambda\mu} = \begin{cases} s_{ijkl} & (ij \leftrightarrow \lambda = 1, 2, 3; \quad kl \leftrightarrow \mu = 1, 2, 3), \\ 2s_{ijkl} & (ij \leftrightarrow \lambda = 1, 2, 3; \quad kl \leftrightarrow \mu = 4, 5, 6), \\ s_{ijkl} & (ij \leftrightarrow \lambda = 4, 5, 6; \quad kl \leftrightarrow \mu = 1, 2, 3), \\ 4s_{ijkl} & (ij \leftrightarrow \lambda = 4, 5, 6; \quad kl \leftrightarrow \mu = 4, 5, 6). \end{cases} \tag{F.18}$$

By analogy with (F.3) this rule can be expressed in the form

$$s_{ijkl} = \frac{s_{\lambda\mu}}{(2-\delta_{ij})(2-\delta_{kl})}. \tag{F.19}$$

Comparing (F.18) and (F.2) we see that each subscript equal to 4, 5 or 6 leads to doubling of the quantity of type ε_{λ} or $s_{\lambda\mu}$ as compared with the corresponding component of the tensor; the same can be seen from (F.3) and (F.19). On the contrary, (F.17) and (F.4) show that the quantities of type σ^{λ} or $c^{\lambda\mu}$ are equal to the corresponding tensor components, no matter what the values of the indices are.

It can be naturally assumed that under transition to another system of coordinates quantities $s_{\mu\nu}$ are transformed as the products of two quantities of type ε_{μ}, while $c^{\mu\nu}$ are transformed as the products of the quantities of type σ^{μ}, i.e. that $s_{\mu\nu}$ and $c^{\mu\nu}$ are respectively the covariant and contravariant components of some second-rank tensors in a six-dimensional space. And indeed, it can easily be verified that the transition to a new coordinate frame is described by the equalities

$$s_{\varkappa'\lambda'} = P^{\mu}_{\varkappa'}P^{\nu}_{\lambda'}s_{\mu\nu}, \tag{F.20}$$

$$c^{\varkappa'\lambda'} = Q^{\varkappa'}_{\mu}Q^{\lambda'}_{\nu}c^{\mu\nu}, \tag{F.21}$$

while a converse transformation—from the new coordinate system to the old one—is performed in accordance with the formulas

$$s_{\mu\nu} = Q^{\varkappa'}_{\mu}Q^{\lambda'}_{\nu}s_{\varkappa'\lambda'}, \tag{F.22}$$

$$c^{\mu\nu} = P^{\mu}_{\varkappa'}P^{\nu}_{\lambda'}c^{\varkappa'\lambda'}. \tag{F.23}$$

Thus, having properly placed the indices of the quantities contained in a certain tensor equality we automatically obtain the rules for the recalculation and the formulas for the transformation of all quantities contained in this equality (if, of course, the equality also contains the known quantities). It is just for this purpose that we use this formal method here.

Some textbooks are insistent on their recommendations for using, when the tensors of the coefficients of elasticity and elastic compliance are referred to

new coordinates, the formulas of the form

$$s_{i'j'k'l'} = c_{i'm}c_{j'n}c_{k'p}c_{l'q}s_{mnpq}. \tag{F.24}$$

but the unwarranted abundance of terms in each of them (81 terms) makes calculations difficult and leads to errors. Formulas (F.20)-(F.23) are evidently more convenient: they have less terms (only 36) and contain just those coefficients of elasticity and elastic compliance which are given in tables.

Although in principle each tensor could be represented either by its covariant or contravariant components, we shall convene to represent strains ε_λ, thermal expansion coefficients α_λ, elastic compliance coefficients $s_{\lambda\mu}$ always by covariant components, and stresses σ^λ, thermoelasticity coefficients β^λ, elasticity coefficients $c^{\lambda\mu}$, by contravariant components. This permits writing all the indices on one level, even though it is less convenient. In the main text of this book all indices are written as subscripts, since this traditional form of notation is used in almost all the existing literature on crystal physics. On the contrary in this Appendix, covariant indices are subscripts, and contravariant ones are superscripts, and the rule of summation according to the Greek indices written unfailingly on different levels is strictly adhered to. An index being a superscript or a subscript defines, as was shown earlier, the relation of the given quantity with the corresponding tensor components, as well as the law of its transformation under a change of the coordinate frame.

To Sec. 52. Matrices *P* and *Q* for Rotation about Axis X_3. To the rotation of a Cartesian coordinate system through angle φ about axis X_3 there corresponds, as it is known, (see Sec. 17) the cosine matrix

$$\| c_{i'k} \| = \begin{Vmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{Vmatrix}. \tag{F.25}$$

Substituting its elements into (F.10) or directly into the expression of the matrices P and Q expanded in terms of $c_{i'k}$, we shall find that matrix P for the rotation of the coordinate system by the angle φ about axis X_3 has the form

$$\| P_\mu^{\lambda'} \| = \begin{Vmatrix} \cos^2\varphi & \sin^2\varphi & 0 & 0 & 0 & \frac{1}{2}\sin 2\varphi \\ \sin^2\varphi & \cos^2\varphi & 0 & 0 & 0 & -\frac{1}{2}\sin 2\varphi \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \cos\varphi & -\sin\varphi & 0 \\ 0 & 0 & 0 & \sin\varphi & \cos\varphi & 0 \\ -\sin 2\varphi & \sin 2\varphi & 0 & 0 & 0 & \cos 2\varphi \end{Vmatrix}, \tag{F.26}$$

while matrix Q differs from it only by the location of the coefficients 1/2 not in the right-hand upper corner but in the left-hand lower corner.

To Sec. 53. Young's Modulus *E* (*q*) and Shear Modulus *G* (*p*, *q*). Quantities of the types ε_λ or σ^λ can be composed of the products of vector components. Indeed, all possible products of two components of one and the same vector (say, $\boldsymbol{q}$) are the components of a symmetric second-rank tensor $\boldsymbol{qq}$:

$$(\boldsymbol{qq})_{ij} = q_i q_j.$$

Passing from a pair of indices $i, j = 1, 2, 3$ to one index $\lambda = 1, \ldots, 6$, the components of the dyad $\boldsymbol{qq}$ can be written down both in the form of covariant

components of a six-dimensional vector

$$(qq)_\lambda = \begin{cases} q_i q_j & \text{for} \quad ij \leftrightarrow \lambda = 1,\ 2,\ 3, \\ 2q_i q_j & \text{for} \quad ij \leftrightarrow \lambda = 4,\ 5,\ 6, \end{cases} \tag{F.27}$$

and in the form of its contravariant components

$$(qq)^\lambda = q_i q_j \quad (ij \leftrightarrow \lambda = 1,\ \ldots,\ 6). \tag{F.28}$$

Which of the forms is best to be chosen, depends on the type of the quantity by which multiplication must be done. If Young's modulus is calculated

$$E\,(q) = (s_{ijkl} q_i q_j q_k q_l)^{-1},$$

the covariant components $s_{\lambda\mu}$ are used as factors; the quantity qq must be correspondingly represented by contravariant components $(qq)^\lambda$, since the summation indice must be at different levels. So,

$$E^{-1}\,(q) = s_{\lambda\mu}\,(qq)^\lambda\,(qq)^\mu. \tag{F.29}$$

The method of notation introduced here is applicable only to symmetric tensors. The products of the components of two different vectors (let us say, p and q) can be used for composing the components of a symmetric second-rank tensor

$$\frac{1}{2}\,(pq + qp)_{ij} = \frac{1}{2}\,(p_i q_j + q_i p_j).$$

Then, as in the preceding case, they can be written down in any of the two forms:

$$\frac{1}{2}\,(pq + qp)_\lambda = \begin{cases} p_i q_j & (ij \leftrightarrow \lambda = 1,\ 2,\ 3), \\ p_i q_j + q_i p_j & (ij \leftrightarrow \lambda = 4,\ 5,\ 6); \end{cases} \tag{F.30}$$

$$\frac{1}{2}\,(pq + qp)^\lambda = \frac{1}{2}\,(p_i q_j + q_i p_j) \quad (ij \leftrightarrow \lambda = 1,\ \ldots,\ 6). \tag{F.31}$$

For calculating the shear modulus $G\,(p,\ q)$ we shall use contravariant components $1/2\,(pq + qp)^\lambda$, since the tabulated values of $s_{\lambda\mu}$ are covariant. Because of the symmetry of tensor s_{ijkl} with respect to the first and second pairs of indices

$$G^{-1}\,(p,\ q) = 4 s_{ijkl} p_i q_j p_k q_l = s_{ijkl}\,(p_i q_j + q_i p_j)\,(p_k q_l + q_k p_l). \tag{F.32}$$

Hence we immediately obtain the formula

$$G^{-1}\,(p,\ q) = s_{\lambda\mu}\,(pq + qp)^\lambda\,(pq + qp)^\mu. \tag{F.33}$$

To Sec. 56. Velocity of Elastic Waves in Crystals. The velocity of a longitudinal elastic wave

$$v = \sqrt{\frac{1}{\rho}\, c_{ijkl} m_i m_j m_k m_l} \tag{F.34}$$

can be apparently expressed in the form

$$v = \sqrt{\frac{1}{\rho}\, c^{\lambda\mu}\,(mm)_\lambda\,(mm)_\mu}\,. \tag{F.35}$$

The indices of the elasticity coefficients being superscripts, we must have the indices of the dyad mm as subscripts and hence there follows the recalculation rule

$$(mm)_\lambda = \begin{cases} m_i m_j & (ij \leftrightarrow \lambda = 1,\ 2,\ 3), \\ 2 m_i m_j & (ij \leftrightarrow \lambda = 4,\ 5,\ 6). \end{cases} \tag{F.36}$$

In a general case the velocity of an elastic wave is

$$v=\sqrt{\frac{1}{\rho}\,c_{ijkl}m_ip_jm_kp_l}. \tag{F.37}$$

Let us introduce a symmetric second-rank tensor $L = 1/2\ (\boldsymbol{mp} + \boldsymbol{pm})$. Evidently

$$v=\sqrt{\frac{1}{\rho}\,c_{ijkl}L_{ij}L_{kl}}=\sqrt{\frac{1}{\rho}\,c^{\lambda\mu}L_\lambda L_\mu} \tag{F.38}$$

with the following recalculation rules

$$L_\lambda=\begin{cases} L_{ij}=m_ip_j & (ij \longleftrightarrow \lambda=1,\ 2,\ 3), \\ 2L_{ij}=m_ip_j+p_im_j & (ij \longleftrightarrow \lambda=4,\ 5,\ 6). \end{cases} \tag{F.39}$$

To Sec. 58. Piezoelectric Coefficients d. The equations of the theory of the piezoelectric effect

$$D_i=\varkappa_{ij}E_j+4\pi\, d_{i\mu}\sigma^\mu, \qquad \varepsilon_\lambda=d_{j\lambda}E_j+s_{\lambda\mu}\sigma^\mu \tag{F.40}$$

point to the recalculation rules for the piezoelectric coefficients. Let us note that Latin indices are still written all on the same level. The recalculation rules

$$d_{i\mu}=\begin{cases} d_{ikl} & (kl \longleftrightarrow \mu=1,\ 2,\ 3), \\ 2\,d_{ikl} & (kl \longleftrightarrow \mu=4,\ 5,\ 6) \end{cases} \tag{F.41}$$

depend only on Greek indices. The transformation formulas for quantities $d_{i\mu}$ are

$$d_{i'\mu'}=c_{i'j}P^\nu_{\mu'}\,d_{j\nu}, \qquad d_{j\nu}=c_{i'j}Q^{\mu'}_\nu\,d_{i'\mu'}. \tag{F.42}$$

To Secs. 61.62. Piezoelectric Coefficients e. The equations of the theory of the piezoelectric effect in the form

$$D_i=\varkappa_{ij}E_j+4\pi e^\mu_i\varepsilon_\mu, \qquad \sigma^\lambda=-e^\lambda_jE_j+c^{\lambda\mu}\varepsilon_\mu \tag{F.43}$$

lead to the following recalculation rules for the coefficients e^μ_i

$$e^\mu_i=e_{ikl} \quad (kl \longleftrightarrow \mu=1,\ \ldots,\ 6) \tag{F.44}$$

and the following transformation formulas

$$e^{\mu'}_{i'}=c_{i'j}Q^{\mu'}_\nu e^\nu_j, \qquad e^\nu_j=c_{i'j}P^\nu_{\mu'}e^{\mu'}_{i'}. \tag{F.45}$$

The recalculation rules and the transformation formulas can be obtained by the same method for other coefficients characterizing piezoelectric properties of crystals.

To Sec. 74. Tensors Characterizing the Non-Linear Effects. The notation of expressions (74.3) with the co- and contravariant indices

$$\tilde{D}_i=\tilde{\varkappa}_{ik}E_k+d_{i\mu}\sigma^\mu+\tilde{R}_{ikl}E_kE_l+2P_{ik\mu}E_k\sigma^\mu+Q_{i\mu\nu}\sigma^\mu\sigma^\nu, \tag{F.46a}$$

$$\varepsilon_\lambda=d_{k\lambda}E_k+s_{\lambda\mu}\sigma^\mu+P_{kl\lambda}E_kE_l+2Q_{k\lambda\mu}E_k\sigma^\mu+L_{\lambda\mu\nu}\sigma^\mu\sigma^\nu \tag{F.46b}$$

determines relations between $P_{ik\mu}$, $Q_{i\mu\nu}$, $L_{\lambda\mu\nu}$ and the components of the corresponding tensors in formulas (74.4): to attain the equality the latter should be multiplied by 2^m, where m is the number of fours, fives or sixes among indices λ, μ, ν. The tensors that characterize non-linear elasticity are determined similarly, see (74.5)-(74.7). With co- and contravariant indices they are written down

in the form

$$c^{\lambda\mu} = c_0^{\lambda\mu} + g^{\lambda\mu\nu}\sigma^{\nu}, \tag{F.47}$$

$$c^{\lambda\mu} = c_0^{\lambda\mu} + C^{\lambda\mu\nu}\varepsilon_{\nu}, \tag{F.48}$$

from which the recalculation rules follow: $C^{\lambda\mu\nu}$ always coincides with C_{ijklmn}, while

$$g_{\nu}^{\lambda\mu} = \begin{cases} g_{ijklmn} & (mn \longleftrightarrow \nu = 1,\ 2,\ 3), \\ 2g_{ijklmn} & (mn \longleftrightarrow \nu = 4,\ 5,\ 6). \end{cases}$$

To Sec. 75. Piezoresistive and Elastoresistive Coefficients. Formulas (75.3) and (75.5) can be expressed in the following form

$$E_j = \rho_{ik}^0 (\delta_{kl} + \Pi_{\mu}^{\lambda}\sigma^{\mu})\, j_l, \tag{F.49}$$

$$E_i = \rho_{ik}^0 (\delta_{kl} + m^{\lambda\mu}\varepsilon_{\mu})\, j_l. \tag{F.50}$$

It is meant here that index λ corresponds to a pair of indices kl, while its being written as a superscript follows from j_k and j_l being vector components*. The position of index μ is determined by the common recalculation rules for σ^{μ} and ε_{μ}.

Formula (F.50) leads to the recalculation rules and transformation formulas for $m^{\lambda\mu}$ exactly coinciding with those obtained earlier for elasticity coefficients $c^{\lambda\mu}$, see (F.17), (F.21) and (F.23). For piezoresistive coefficients Π_{μ}^{λ}, (F.49) leads to recalculation rules (75.7) to which there correspond peculiar transformation formulas

$$\Pi_{\mu'}^{\lambda'} = Q_{\nu}^{\lambda'} P_{\mu'}^{\varkappa} \Pi_{\varkappa}^{\nu}, \quad \Pi_{\varkappa}^{\nu} = P_{\lambda'}^{\nu} Q_{\varkappa}^{\mu'} \Pi_{\mu'}^{\lambda'}. \tag{F.51}$$

To Sec. 77. Piezooptical, Elastooptical and Kerr's Coefficients. For writing down the equations of the piezooptical effect with their co- and contravariant indices the choice of the recalculation rules for changing the optical indicatrix is highly important. The recalculation rules corresponding to the form ζ^{λ} are more widely used; for example, they were used by J. F. Nye (1957). The equations

$$\zeta^{\lambda} = \pi_{\mu}^{\lambda}\sigma^{\mu}, \tag{F.52}$$

$$\zeta^{\lambda} = p^{\lambda\mu}\varepsilon_{\mu}. \tag{F.53}$$

correspond to them.

The recalculation rules for π_{μ}^{λ} are the same as for the piezoresistive coefficients Π_{μ}^{λ}. Therefore transformation formulas (F.51) are also applicable to coefficients π_{μ}^{λ}. The position of indices of the coefficients $p^{\lambda\mu}$ is the same as of the elastoresistive coefficients $m^{\lambda\mu}$ and the elasticity coefficients $c^{\lambda\mu}$. This leads to recalculation rules (F.17) and transformation formulas (F.21) and (F.23).

Kerr's effect is considered in the same way. Since for the dyad EE the formula

$$(EE)^{\mu} = E_k E_l \quad (kl \longleftrightarrow \mu = 1,\ \ldots,\ 6), \tag{F.54}$$

is used, the recalculation rules and transformation formulas applicable to Kerr's coefficients K_{μ}^{λ} and to the piezooptical coefficients π_{μ}^{λ} are the same.

---

* Had the recalculation rules corresponded to index λ as a subscript, formulas (F.49) and (F.50) would give doubled values of piezoresistive increments to j_k in cases when $l \neq k$.

To Sec. 77. Electrooptical Coefficients. The rules accepted for the recalculation of ζ^{λ} for changing the optical indicatrix lead to writing down the electrooptical effect equation (77.16) in the form

$$\zeta^{\lambda} = r_k^{\lambda} E_k \tag{F.55}$$

and correspondingly to the recalculation rules for the electrooptical coefficients (77.18). The transformation formulas for r_k^{λ} are similar to those of (F.45) for piezoelectrical coefficients e_i^{μ}:

$$r_{k'}^{\lambda'} = Q_{\mu}^{\lambda'} c_{k'l} r_l^{\mu}, \qquad r_l^{\mu} = P_{\lambda'}^{\mu} c_{k'l} r_{k'}^{\lambda'}. \tag{F.56}$$

REFERENCES

Aero, E. L., Kuvshinski, E. V. (1960) *Fiz. Tverd, Tela*, 2, 1399.

Agranovich, V. M., Ginzburg, V. L. (1966) *Spatial Dispersion in Crystal Optics and in the Theory of Excitons*, Interscience, New York.

Agranovich, V. M., Ginzburg, V. L. (1972) *JETP*, 63, 838.

Akhmanov, S. A. (1969) In: *Quantum Electronics—Small Encyclopedia*, Sov. Encyclopedia, Moscow, 119 (in Russian).

Akhmanov, S. A., Khokhlov, R. V. (1964) *Problems of Non-Linear Optics*, *VINITI*, Moscow (in Russian).

Akivis, M. A., Gol'dberg, V. V. (1969) *Tensor Calculus*, Nauka, Moscow (in Russian).

Alexandrov, K. S. (1956) *Crystallographia*, 1, 718.

Alexandrov, K. S. (1958) *Crystallographia*, 3, 620.

Alexandrov, K. S. (1975) In: *Problems of Contemporary Crystallography*, Ed.: B. K. Vainstein and A. A. Chernova, Nauka, Moscow, 327 (in Russian).

Alexandrov, K. S., Zinenko, V. I., Mikhelson, L. M., Sirotin, Yu. I. (1969) *Crystallographia*, 14, 327.

Alexandrov, K. S., Ryzhova, T. V. (1961) *Crystallographia*, 6, 289.

Alexandrov, V. N. (1970) *Crystallographia*, 15, 996.

Ambartsumyan, S. A. (1967) *Theory of Anisotropic Plates*, Nauka, Moscow (in Russian).

Andronov, A. A. (1960) Transactions of Higher Educational Institutions: *Radiophysics*, 3, 45.

Astrov, D. N. (1960) *JETP*, 38, 984.

Auld, B. (1973) *Acoustic Fields and Waves in Solids*, Vol I, II, Wiley, New York.

Barfoot, J. C., (1967) *Ferroelectrics. An Introduction to the Physical Principles.* Princeton, New Jersey; Toronto.

Barkovski, L. M. (1970) *Transactions of the Belorussian University*, Ser. 1, 2, 42.

Beloborodova, V. A., Rovenskaya, O. S., Sirotin, Yu. I. (1972) *Crystallographia*, 17, 1187.

Belov, K. F. (1959) *Magnetic Transformations*, Physmatgiz, Moscow (in Russian).

Belov, K. F., Belyanchikova, M. A., Levitin, R. Z. et al. (1965) *Rare-Earth Ferro- and Antiferromagnetics*, Nauka, Moscow (in Russian).

Belov, N. V. (1947) *Structure of Ionic Crystals and Metallic Phases*, Publication of the Ac. Sci. USSR, Moscow (in Russian).

Belov, N. V. (1951) *Structural Crystallography*, Publication of the Ac. Sci. USSR, Moscow (in Russian).

Belov, N. V. (1957) *Crystallographia*, 2, 678.

Belov, N. V. (1958) *Crystallographia*, 3, 246.

Belov, N. V. (1976) *Notes on Structural Mineralogy*. Nedra, Moscow.

Belov, N. V. (1964) *Coloured Symmetry*, Pergamon Press, 175.

Belov, N. V., Neronova, N. N., Smirnova, T. S. (1957) *Crystallographia*, 2, 315.

Belov, N. V., Tarkhova, T. N. (1956) In: A. V. Shubnikov, N. V. Belov (1964) *Coloured Symmetry*, Pergamon Press, 211.
Belova, E. N., Belov, N. V., Shubnikov, A. V. (1948). *Dokl. Akad. Nauk, USSR*, **63**, 669.
Berestetski, V. B., Lifshits, E. M., Pitayevski, L. P. (1968) *Relativity Quantum Theory*, Part I, Nauka, Moscow (in Russian).
Bhagavantam, S., Venkatarayudu, T. (1962) *Theory of Groups and Its Application to Physical Problems*, Acad. Press, New York.
Bhagavantam, S. (1966) *Crystal Symmetry and Physical Properties*, Acad. Press, London—New York.
Bhagavantam, S., Suryanarayana, D. (1949) *Acta Crystallogr.*, **2**, 21.
Bier, G. L., Pikus, G. E. (1972) *Symmetry and Strain Effects in Semiconductors*, Nauka, Moscow.
Birss, R. (1962) *Proc. Phys. Soc.*, **79**, 946.
Birss, R. (1964) *Symmetry and Magnetism*, North Holland Publ., Amsterdam.
Blistanov, A. A., Petrakov, V. S., Sorokin, N. G., Chizhikov, S. I., Shaskolskaya, M. P. (1977) *JETP Lett.*, **26**, 141.
Bloembergen, N. (1966) *Non-Linear Optics*. Benjamin, New York.
Bokyi, G. B. (1940) In: *Proceedings of the Lab. of Crystallography of the Ac. Sci. USSR*, **2**, 13.
Bokyi, G. B. (1971) *Crystal Chemistry*. 2nd ed., revised, Nauka, Moscow.
Bokut', B. V., Serdyukov, A. N. (1971) *JETP*, **61**, 1808.
Bokut', B. V., Serdyukov, A. N., Fedorov, F. I. (1970) *Crystallographia*, **15**, 1002.
Boldyrev, A. K. (1934) *Crystallography*. 3rd ed., revised and enlarged, Gorgeonefteizdat, Leningrad (in Russian).
Boldyrev, A. K. (1936) *Amer. Mineral.*, **21**, 731.
Borisenko, A. I., Tarapov, I. E. (1966) *Vector Analysis and the Principles of Tensor Calculus*, Vysshaya Shkola, Moscow (in Russian).
Born, M. (1965) *Optik*. Springer Verlag, Heidelberg.
Born, M., Wolf, E. (1964) *Principles of Optics*. Pergamon Press.
Born, M., Huangh, K. (1966) *Dynamical Theory of Crystal Lattices*, Clarendon Press, London.
Boyle, L. L., Lawrenson, J. E., (1972) *Acta Crystallogr.*, **A28**, 485.
Borovik-Romanov, A. S. (1959) *JETP*, **36**, 1954.
Borovik-Romanov, A. S. (1960) *JETP*, **38**, 1088.
Brout, R. (1965) *Phase Transitions*, Benjamin, New York.
Brewster, D. (1818) *Trans. Roy. Soc. Edinb.*, **8**, 281.
Buerger, M. J., (1942) *X-ray Crystallography*, New York, London.
Buerger, M. J. (1965) *Elementary Crystallography*, Wiley, New York.
Buerger, M. J. (1970) *Contemporary Crystallography*, McGraw Hill, New York.
Burkhardt, J. (1947) *Die Bewegungsgruppen der Kristallographie*, Verlag Birkhäuser, Basel.
Butabayev, Sh. M., Sirotin, Yu. I. (1972) *Crystallographia*, **17**, 1181.
Butabayev, Sh. M., Sirotin, Yu. I. (1973) *Crystallographia*, **18**, 195.
Butabayev, Sh. M., Sirotin, Yu. I. (1971) In: *Proc. of TIIIMSKH*, issue 78, 207.
Butabayev, Sh. M., Smyslov, I. I. (1971) *Crystallographia*, **16**, 796.
Cady, W. (1946) *Piezoelectricity*. An Introduction to the Theory and Applications of Electromechanical Phenomena in Crystals.
Cady, W. G. (1964) *Piezoelectricity*, Dover, New York.
Chaskolskaya, M. P. (1959) *Les Cristaux*, Edition on langues entrangeres, Moscou.
Chern, M. J., Phillips, R. A. (1970) *J. Opt. Soc. Amer.*, **60**, 120.
Cochran, W., Zia, A. (1968) *Phys. Stat. Solidi*, **25**, 273.
Coker, E. G., Filon, L. N. (1931) *Treatise on Photoelasticity*. Cambridge Univ. Press, London.

Curie, M. (1955) *Pierre Curie.* ed. Denoel, Paris.
Curie, P. *Oeuvres choisis*, Paris.
De Groot, S. R., Mazur, P. (1962) *Non-Equilibrium Thermodynamics*, North Holland Publ., Amsterdam.
Delone, B. N., Galyulin, R. V., Shtogrin, M. I. (1974) *Bravais Theory and Its Generalization for n-Dimensional Lattices.* In: Au. Bravais. *Selected Scientific Works*, Nauka, Moscow.
Delone, B. N., Padurov, N. N., Alexandrov, A. A. (1934) *Mathematical Foundations of the Structural Analysis of Crystals*, Gostekhizdat, Leningrad (in Russian).
Dieulesaint, E., Royer, D. (1974) *Ondes elastiques dans les solides*, Ed. Masson, Paris.
Ditchburn, R. W. (1963) *Light*, Blackie and Son, Ltd., London.
Donnay, J. D. H. (1973) *Crystal Tables* (*Determinative tables*). 3rd ed., Ed. Amer. Crystallogr. Assoc., New York.
Döring, W. (1958) *Ann. Physik.* Ser. 7, **1**, 104.
Durelli, A. J., Riley, W. F. (1965) *Introduction to Photomechanics*, Prentice Hall Inc., Englewood Cliffs.
Dvorak, W. (1971) *Phys. Stat. Solidi* B, **45**, 147.
Dvorak, W., Petzelt, J. (1971) *Czech. J. Phys.* B., **21**, 1147.
Dzyaloshinski, I. E., Lifshits, E. M. (1957) *JETP*, **33**, 299.
Dzyaloshinski, I. E. (1957) *JETF.* **33**, 807.
Dzyaloshinski, I. E. (1959) *JETF.* **37**, 881.
Dzyaloshinski, I. E. (1964) *JETF.* **46**, 1420.
Dzyaloshinski, I. E. (1964a) *JETF.* **47**, 336, 992.
Ehyshima, K., Ogawa, T. (1971) *J. Phys. Soc. Japan*, **31**, 308.
Fabelinski, I. L. (1965) *Molecular Scattering of Light*, Nauka, Moscow (in Russian).
Faddeyev, D. K. (1961) *Tables of the Principal Unitary Representation of Fedorov's Groups*, Publ. of the Ac. Sci. USSR, Moscow (in Russian).
Farneel, G. W. (1961) *Canad. J. Phys.*, **39**, 65.
Fedorov, E. S. (1949) *Symmetry and Structure of Crystals*, Publ. of the Ac. Sci. USSR, Moscow (in Russian).
Fedorov, F. I. (1958) *Optics of Anisotropic Bodies*, Publ. of the Ac. Sci. Belorus. SSR, Minsk (in Russian).
Fedorov, F. I. (1959) *Optics and Spectroscopy*, **6**, 377.
Fedorov, F. I. (1959a) *Optics and Spectroscopy*, **6**, 85.
Fedorov, F. I. (1968) *Theory of Elastic Waves in Crystals.* Plenum Press, New York.
Fedorov, F. I. (1970) *Crystallographia*, **15**, 631, 638.
Fedorov, F. I. (1975) *Theory of Gyrotropic Bodies*, Publ. of the Ac. Sci. Belorus. SSR, Minsk (in Russian).
Feynman Lectures on Physics (1964). Wesley Publ. Co. Inc., Reading, Massachussets.
Fieshi, R., Fumi, F. G. (1953) *Nuovo Cimento*, **10**, 65.
Flint, E. E. (1956). *Practical Handbook on Geometrical Crystallography*, Gosgeoltekhizdat, Moscow (in Russian).
Foepple, L., Menkh, E. (1966) *Practice of Optical Modelling*, Nauka, Moscow (in Russian).
Fumi, F. G. (1951) *Phys. Rev.*, **83**, 1274.
Fumi, F. G. (1952) *Acta Crystallogr.*, **5**, 44, 691.
Fumi, F. G. (1952a) *Nuovo Cimento*, **9**, 739.
Fumi, F. G. (1952b) *Phys. Rev.*, **86**, 561.
German, V. L. (1945) *Papers of the Ac. Sci. USSR*, **48**, 95.
Ginzburg, V. L. (1949) *Usp. Fiz. Nauk*, **38**, 430.
Gol'denblat, I. I. (1959) *Non-Linear Problems of the Theory of Elasticity*, Nauka, Moscow (in Russian).

Goldsmid, R. J., Ed. (1975) *Problems in Solid State Physics*, Acad. Press, New York.
Groth, P. (1895) *Physikalische Kristallographie und Einleitung in die kristallographische Kenntniss der wichtigsten Substanzen*, Berlin.
Gufan, Yu. M. (1971) *Fiz. Tverd. Tela*, **13**, 225.
Gufan, Yu. M., Sakhnenko, V. P. (1972) *Fiz. Tverd. Tela*, **14**, 1915.
Gufan, Yu. M., Sakhnenko, V. P. (1972a) JETP, **63**, 1909.
Gufan, Yu. M., Sakhnenko, V. P., Sirotin, Yu. I. (1974) *Crystallographia*, **14**, 21.
Haase, R. (1963) *Thermodynamik der irreversiblen Prozesse*. Dr. Dietrich Steinkopff Verlag, Darmstadt.
Hammermesh, M. (1960) *Group Theory and its Application to Physical Problems*. Addison-Wesley, Reading, Mass.
Hartmann, E. (1973) *Magyar Fizikai Folyirat*, **XXI**, 357.
Heine, W. (1960) *Group Theory in Quantum Mechanics*, Pergamon Press, London.
Henneke, E. G., Green, R. E. (1969) *J. Acoust. Soc. Amer.*, **45**, 1367.
Hermann, C. (1934) *Zs. Kristallogr.*, **89**, 32.
Hobden, M. V. (1968) *Acta Crystallogr.*, A, **24**, 676.
Hobden, M. V. (1969) *Acta Crystallogr.*, A, **25**, 633.
Hruska, K., Khogali, A. (1971) *Trans. IEEE SU*, **18**, 171.
Iliushin, A. A. (1971) *Mechanics of Continuous Media*, Publication of the MSU, Moscow (in Russian).
Indenbom, V. L. (1959) *Crystallographia*, **4**, 619.
Indenbom, V. L. (1960) *Crystallographia*, **15**, 115.
Indenbom, V. L. (1960a) *Transactions of the Ac. Sci. USSR*, Ser. Phys., **24**, 1180.
Indenbom, V. L., Belov, N. V., Neronova, N. N. (1960) *Crystallographia*, **5**, 497.
Indenbom, V. L., Silvestrova, I. M., Sirotin, Yu. I. (1956) *Crystallographia*, **1**, 599.
International Tables for X-Ray Crystallography (1965, 1966, 1968), Vol. I, II, III. Kynoch Press, Birmingham.
Ioffe, A. F. (1932) *Physics of Crystals*, GTTI, Leningrad.
IRE Standards on Piezoelectric Crystals (1949) *Proc. IRE*. **37**, 1378; (1957), *Proc. IRE*. **45**, 354; (1958). *Proc. IRE*. **46**, 765; (1961). *Proc. IRE*, **49**, 1162.
Ivanov, N. R., Konstantinova, A. F. (1970) *Crystallographia*, **15**, 490.
Izyumov, Yu. A., Ozerov, R. P. (1966) *Magnetic Neutronography*, Nauka, Moscow (in Russian).
Jahn, H. A. (1949) *Acta Crystallogr.*, **2**, 33.
Jahnke, E., Emde, F., Loesch, F. (1933) *Funktionentafeln*. Dover Publ. Leipzig-Berlin, Teubner; New York.
Janik, L., Hruska, K. (1970) *Czech. J. Phys.* B., **20**, 202.
Jona, F., Shirane, G. (1962) *Ferroelectric Crystals*, Pergamon Press, London.
Känzig, W. (1957) *Ferroelectrics and Antiferroelectrics in Solid State Physics*, vol. 4.
Karandeyev, V. V. (1913) *Crystal Optics*, Publication of the Higher Courses for Women, Moscow (in Russian).
Khachaturyan, A. G. (1965) *Dokl. Akad. Nauk SSSR*, **165**, 1284.
Khachaturyan, A. G. (1974) *Theory of Phase Transformations and the Structure of Solid Solutions*, Nauka, Moscow (in Russian).
Khatkevich, A. G. (1962) *Crystallographia*, **7**, 742.
Khatkevich, A. G. (1962a) *Crystallographia*, **7**, 916.
Kittel, Ch. (1975) *Introduction to Solid State Physics*. Wiley, New York.
Kleber, W. (1977) *Einführung in die Kristallographie*, 13 Auflage, VEB Verlag Technik, Berlin.
Kleber, W., Meyer, K., Schoenborn, W. (1968) *Einführung in die Kristallphysik*, Akad. Verlag, Berlin.

Kleiner, W. H. (1966) *Phys. Rev.*, **142**, 318.
Kleiner, W. H. (1969) *Phys. Rev.*, **182**, 705.
Klimontovich, Yu. L. (1966) *Quantum Generators and Non-Linear Optics*, Prosveshchenie, Moscow (in Russian).
Knox, R. S., Gold, A. (1964) *Symmetry in the Solid State*, W. A. Benjamin Inc., New York.
Konstantinova, A. F., Ivanov, N. R., Grechushnikov, B. N. (1969) *Crystallographia*, **14**, 283.
Koptsik, V. A. (1958) In: W. Wooster. *Practical Handbook on Crystal Physics*. IL, Moscow.
Koptsik, V. A. (1960) *Crystallographia*, **5**, 932.
Koptsik, V. A. (1960) *Shubnikov groups*, Publication of the MGU, Moscow (in Russian).
Koptsik, V. A. (1967) *Crystallographia*, **12**, 826.
Koptsik, V. A., Ryabchikov, S. A., Sirotin, Yu. I. (1977) *Crystallographia*, **22**, 229.
Koptsik, V. A., Sirotin, Yu. I. (1961) *Crystallographia*, **5**, 766.
Kornfeld, M. I., Chudinov, A. A. (1957) *JETP*, **33**, 33.
Kostov, I. (1963) *Crystallography*. Sophia (in Bulgarian).
Kovalev, O. V. (1961) *Irreducible Representations of Space Groups*, Publication of the Ac. Sci. Ukr. SSR, Kiev (in Russian).
Kozyrev, C. P., Gil'varg, A. B., Grechushnikov, B. N. et al. (1973) *Crystallographia*, **18**, 1292.
Krinchik, G. S., Chetkin, M. V. (1969) *Usp. Fiz. Nauk*, **98**, 3.
Krishnan, R. S. (1958) In: *Progress in Crystal Physics*, Visvanathan, Vol. 1, Madras.
Krishnan, R. S., Radha, V., Gopal, E. S. R. (1971) *J. Phys. D: Appl. Phys.*, **4**, 171.
Kuvshinski, E. V., Aero, E. L. (1963) *Fiz. Tverd. Tela*, **5**, 2529.
Landau, L. D. (1937) *JETP*, **7**, 19.
Landau, L. D., Lifshits, E. M. (1976) *Mechanics of Continuous Media*, Pergamon Press, Oxford, New York.
Landau, L. D., Lifshits, E. M. (1976) *Electrodynamics of Continuous Media*, Pergamon Press, Oxford, New York.
Landau, L. D., Lifshits, E. M. (1965) *Theory of Elasticity*, Pergamon Press, Oxford, New York.
Landau, L. D., Lifshits, E. M. (1973) *The Classical Theory of Fields*, Pergamon Press, Oxford, New York.
Landau, L. D., Lifshits, E. M. (1976) *Quantum Mechanics*, Pergamon Press, Oxford, New York.
Landau, L. D., Lifshits, E. M. (1976) *Statistical Physics*, Pergamon Press, Oxford, New York.
Landolt-Boernstein (1966, 1969, 1971) Numerical Data and Functional Relationships in Science and Technology, New Series, Groups III: *Crystal and Solid State Physics*, Vol. I, II, III, Berlin-New York, Springer Verlag, Heidelberg.
Landsberg, G. S. (1957) *Optics*, Gostekhizdat, Moscow (in Russian).
Leibenson, L. S. (1947) *A Course in the Theory of Elasticity*, Gostekhizdat, Moscow (in Russian).
Leibfried, G. (1961) Gittertheorie der mechanischen und thermischen Eigenschaften der Kristall. In: *Handbuch der Physik*, Bd. VII, Teil 2, Berlin, Springer Verlag, Heidelberg.
Lekhnitski, S. G. (1947) *Anisotropic Plates*, Gostekhizdat, Moscow.
Lekhnitski, S. G. (1950) *Theory of Elasticity of an Anisotropic Body*, Gostekhizdat, Moscow (in Russian).
Lekhnitski, S. G. (1971) *Twisting of Anisotropic and Non-Homogeneous Rods*, Nauka, Moscow (in Russian).

Lemanov, V. V., Smolenski, G. A. (1972) *Usp. Fiz. Nauk*, **103**, 455.
Levanyuk, A. P., Sannikov, D. G. (1970) *Usp. Fiz. Nauk*, **12**, 2997.
Levanyuk, A. P., Sannikov, D. G. (1971) *JETP*, **60**, 1109.
Levanyuk, A. P., Sannikov, D. G. (1974) *Usp. Fiz. Nauk*, **112**, 561.
Lifshits, E. M. (1941) *JETP*, **11**, 255.
Lifshits, E. M., Rosenzweig, L. N. (1947) *JETP*, **17**, 783.
Lipson, H., Cochran, W. (1966) *The Crystalline State. The Determination of Crystal Structures*, London.
Lokhin, V. V., Sedov, L. I. (1963) *Applied Mathematics and Mechanics*, **27**, 393.
Lonsdale, K. (1948) *Crystals and X-Rays*. Bell and Sons, Ltd., London.
Love, A. E. H. (1944) *A Treatise on the Mathematical Theory of Elasticity*, New York.
Lurie, A. I. (1955) *Space Problems of the Theory of Elasticity*, Gostekhizdat, Moscow (in Russian).
Lurie, A. I. (1970) *Theory of Elasticity*, Nauka, Moscow (in Russian).
Maloletkin, G. N., Fomin, V. L. (1972) *Tensor Bases in Crystal Physics*, Publication of the LSU, Leningrad (in Russian).
Mason, W. P. (1950) *Piezoelectric Crystals and Their Application to Ultrasonics*. Princeton, New Jersey, Van Nostrand.
Mason, W. P. (1964) *Physical Acoustics, Principles and Methods*. Vol. 1, p. 8. Acad. Press, New York.
Mason, W. P. (1966) *Crystal Physics of Interaction Processes*. Acad. Press, New York.
Markovski, V. Yu., Polukhin, P. I., Shaskolskaya, M. P. (1956) In: Polarization-Optical Method of the Investigation of Stresses. Ed: N. I. Pirogovski, *Publication of the LSU*, Leningrad (in Russian).
Melankholin, N. M. (1970) *Methods of Investigation of the Optical Properties of Crystals*, Nauka, Moscow.
Mikhelson, L. M., Sirotin, Yu. I. (1969) *Crystallographia*, **14**, 573.
Miller, G. F., Musgrave, M. J. P. (1956) *Proc. Roy. Soc. A.*, **236**, 352.
Minnigerode, B. (1887) *Neues Jahrb. Mineral.*, **5**, 145.
Musgrave, M. J. P. (1954) *Proc. Roy. Soc.* A., **226**, 356.
Musgrave, M. J. P. (1970) *Crystal Acoustics*, Holden Day Inc. Publ., San Francisco.
Mustel, E. P., Parygin, V. N. (1970) *Methods of the Modulation and Scanning of Light*, Nauka, Moscow (in Russian).
Naish, V. E. (1963) *Transactions of the Ac. Sci. USSR*, Ser. Phys., **27**, 1496.
Nelson, D. F., Lax, M. (1970) *Phys. Rev. Lett.*, **24**, 379.
Neumann, F. (1885) *Vorlesungen über die Theorie der Elastizität*. Acad. Verlag, Leipzig.
Novozhilov, V. V. (1958) *Theory of Elasticity*, Sudpromgiz. Leningrad (in Russian).
Nye, J. F. (1957) *Physical Properties of Crystals*. Clarendon Press, Oxford.
Nye, J. F. (1964) *Physical Properties of Crystals. Their Representation by Tensors and Matrices*. Oxford.
Ohmachi, Y., Uchida, N., Nitzeki, N. (1972) *J. Acoust. Soc. Amer.*, **51**, 164.
Orlov, R. Yu. (1969) Trans. of the Higher Educational Institutions, *Radiophysics*, **12**, 1351.
Pace, E. G., Saunders, G. A. (1971) *J. Phys. Chem. Solids*, **32**, 1585.
Pal'mov, V. A. (1964) *Applied Mathematics and Mechanics*, **28**, 400.
Pantulu, P. V., Sudarshan, E. (1970) *J. Phys.* C: Solid State Phys., **3**, 60.
Pekara, A. (1973) New Aspect of Optics, *Sov. Radio*, Moscow (in Russian).
Perelomova, N. V., Tagieva, M. M. (1972) *Problems in Crystal Physics*. Ed.: M. P. Shaskolskaya, Nauka, Moscow (in Russian).
Perfilova, V. E., Sonin, A. S., Sirotin, Yu. I. (1969) *Crystallographia*, **14**, 157.
Petrashen', M. I., Trifonov, E. D. (1967) *Use of Group Theory in Quantum Mechanics*, Nauka, Moscow (in Russian).

Phillips, F. C. (1971) *An Introduction to Crystallography*. Oliver and Boyd, New York.
Pine, A. S. (1971) *J. Acoust. Soc. Amer.*, **49**, 1026.
Pleshakov, V. F., Sirotin, Yu. I. (1966) *Applied Mathematics and Mechanics*, **30**, 243.
Pockels, F. (1894) *Abb. Göttinger Ges. d. Wiss.*, **39**, 99.
Pockels, F. (1906) *Lehrbuch der Kristalloptik*, Verlag Teubner, Leipzig.
Popov, G. M., Shafranovski, I. I. (1972) *Crystallography*, Vysshaya Shkola, Moscow (in Russian).
Ramachandran, G. N., Ramaseshan, S. (1961) Crystal Optics.—In: *Handbuch der Physik*, Bd. 25/1, Springer Verlag, Berlin.
Ranganath, G. S. (1972) *Proc. Indian Acad. Sci.* A, **75**, 237.
Ranganath, G. S., Ramaseshan, S. (1969) *Proc. Indian Acad. Sci.* A., **70**, 275.
Schubert, M., Wilhelmi, B. (1971) *Einführung in die nichtlineare Optik*, B. G. Teubner, Leipzig.
Sedov, L. I. (1962) *Introduction to Mechanics of Continuous Media*. Physmatgiz, Moscow (in Russian).
Sedov, L. I. (1970). *Mechanics of Continuous Media*, Nauka, Moscow.
Shafranovski, I. I. (1968) *Lectures on Crystal Morphology*, Vysshaya Shkola, Moscow (in Russian).
Shafranovski, I. I. (1968a) *Symmetry in Nature*, Nedra, Moscow (in Russian).
Shaskolskaya, M. P. (1976) *Crystallography*, Vysshaya Shkola, Moscow (in Russian).
Shaskolskaya, M. P. (1978) *Crystals*, Nauka, Moscow (in Russian).
Shaskolskaya, M. P. (1978a) *Notes on the Properties of Crystals*. Nauka, Moscow.
Shaskolskaya, M. P. (1969-1972) *Handbook of Physical Crystallography*, subjects 1-7, Publ. of the Moscow Institute of Steel and Alloys, Moscow (in Russian).
Shcherbakov, V. A. (1972) News of the MGU.—*Ser. Phys. and Astronomy*, **2**, 195.
Sheludev, I. S. (1975) *Elektrische Kristalle*, Akad. Verlag, Berlin.
Shouten, J. A. (1951) *Tensor Analysis for Physicists*, Clarendon Press, Oxford.
Shubnikov, A. V. (1940) *Symmetry: Laws of Symmetry and Their Application in Science, Technology and Applied Arts*, Publication of the Ac. Sci. USSR, Moscow (in Russian).
Shubnikov, A. V. (1949) *Transactions of the Ac. Sci. USSR*, Ser. Phys., **13**, 347.
Shubnikov, A. V., Belov, N. V. (1964) *Coloured Symmetry*. Pergamon Press, London.
Shubnikov, A. V. (1956) *Crystallographia*, **1**, 95.
Shubnikov, A. V. (1956a) *Usp. Fiz. Nauk*, **59**, 594.
Shubnikov, A. V. (1958) *Fundamentals of Optical Crystallography*. Publication of the Ac. Sci. USSR, Moscow (in Russian).
Shubnikov, A. V. (1960) *Encyclopaedic Physical Dictionary*, Vol. 2, 533.
Shubnikov, A. V. (1975) *Selected Works on Crystallography*, Nauka, Moscow.
Shubnikov, A. V., Koptsik, V. A. (1972) *Symmetry in Science and Art*, Nauka, Moscow.
Shubnikov, A. V., Flint, E. E., Bokyi, G. B. (1949) *Fundamentals of Crystallography*, Publication of the Ac. Sci. USSR, Moscow (in Russian).
Shuvalov, L. A. (1959) *Crystallographia*, **4**, 399.
Shuvalov, L. A. (1963) *Crystallographia*, **8**, 617.
Shuvalov, L. A. (1970) *J. Phys. Soc. Japan*, **28**, 38.
Shuvalov, L. A., Ivanov, N. R. (1964) *Crystallographia*, **9**, 363.
Shuvalov, L. A., Ivanov, N. R., Chikhladze, O. A. et al. (1973) *Crystallographia*, **18**, 1207.
Sirotin, Yu. I. (1956) *Crystallographia*, **1**, 708.
Sirotin, Yu. I. (1960) *Crystallographia*, **5**, 171.
Sirotin, Yu. I. (1960a) *Dokl. Akad. Nauk SSSR*, **133**, 2.
Sirotin, Yu. I. (1961) *Crystallographia*, **6**, 333.

Sirotin, Yu. I. (1962) *Crystallographia*, **7**, 83.
Sirotin, Yu. I. (1963) *Crystallographia*, **8**, 259.
Sirotin, Yu. I. (1964) *Applied Mathematics and Mechanics*, **28**, 653.
Sirotin, Yu. I. (1965) *Crystallographia*, **10**, 15.
Sirotin, Yu. I. (1967) *Crystallographia*, **12**, 208.
Sirotin, Yu. I., Mikhelson, L. M. (1968) *Fiz. Tverd. Tela*, **10**, 1843.
Sirotin, Yu. I., Mikhelson, L. M. (1969) *Transactions of the Ac. Sci. USSR*,— Ser. Phys., **33**, 178.
Sirotin, Yu. I., Rovenskaya, O. S. (1973) *Vestnik* (Newsletter) of the MGU, **1**, 69.
Sirotin, Yu. I., Yanusova, L. G. (1977) Manuscript at *VINITI*, No. 4415/77.
Slater, J. C. (1967) *Insulators, Semiconductors, Metals*. McGraw-Hill Book, New York.
Smagin, A. G., Yaroslavski, M. I. (1970) *Piezoelectricity of Quartz and Quartz Resonators*, Energia, Moscow (in Russian).
Smith, G. F. (1962) *Arch. Rational. Mech. Anal.*, **10**, 103.
Smith, G. F. (1970) *Ann. New York Acad. Sci.*, **172**, 57.
Smith, G. F., Kiral, E. (1969) *Rend. Circ. Mat. Palermo*, ser. 2, **18**, 5.
Smith, G. F., Rivlin, R. S. (1964) *Arch. Rational. Mech. Anal.*, **15**, 169.
Smith, G. F., Smith, M. M., Rivlin, R. S. (1963) *Arch. Rational. Mech. Anal.*, **12**, 93.
Smolenski, G. A., Bokov, V. A., Isupov, V. A. et al. (1971) *Ferroelectrics and Antiferroelectrics*, Nauka, Moscow (in Russian).
Smolenski, G. A., Krainik, N. N. (1968) *Ferroelectrics and Antiferroelectrics*, Nauka, Moscow (in Russian).
Smolenski, G. A., Pisarev, R. V., Sinii, I. G. et al. (1972) *Trans. of the Ac. Sci. USSR*, Ser. Phys., **36**, 1219.
Sonin, A. S. (1976) *Discussions on Crystal Physics*, Atomizdat, Moscow (in Russian).
Sonin, A. S., Vasilevskaya, A. S. (1971) *Electrooptical Crystals*, Atomizdat, Moscow (in Russian).
Sonin, A. S., Zheludev, I. S. (1959) *Crystallographia*, **4**, 487.
Sonin, A. S., Strukov, B. A. (1970) *Introduction to Ferroelectricity*, Vysshaya Shkola, Moscow (in Russian).
Steenrod, N. E., Chinn, E. G. (1966) *First Concepts of Topology*. Random House, New York-Toronto.
Streitwolff, H.-W. (1967) *Gruppentheorie in der Festkörperphysik*, Akad. Verlag, Leipzig.
Sushchinski, M. M. (1969) *Spectrums of Combination Scattering of Molecules and Crystals*, Nauka, Moscow (in Russian).
Tavger, B. A. (1958) *Crystallographia*, **3**, 339.
Tavger, B. A., Zaitsev, V. I. (1956) *JETP*, **30**, 564.
Thurston, P. (1964) In: *Physical Acoustics*, W. P. Mason. Vol. I, p. A., Acad. Press, New York.
Thurston, P. (1967) In: *Physical Acoustics*, W. P. Mason. Vol. I, p. B., Acad. Press, New York.
Turov, E. (1963) *Physical Properties of Magnetically Ordered Crystals*, Publication of the Ac. Sci. USSR, Moscow (in Russian).
Uzdalev, A. I. (1967) *Some Problems of Thermal Elasticity of an Anisotropic Body*. Publ. of the Saratov Univ., Saratov (in Russian).
Vaks, V. G. (1973) *Introduction to Microscopic Theory of Ferroelectrics*, Nauka, Moscow (in Russian).
Varikash, V. M., Khachatryan, Yu. M. (1969) *Selected Problems on the Solid State Physics*, Publ. of Vysheishaya Shkola, Minsk (in Russian).
Vasiliev, D. M. (1972) *Physical Crystallography*, Metallurgia, Moscow (in Russian).
Vedam, K., Srinavasam, R. (1967) *Acta Crystallogr.*, **22**, 630.

Vinberg, E. B., Gufan, Yu. M., Sakhnenko, V. P., Sirotin, Yu. I. (1974) *Crystallographia*, **19**, 21.
Viswanathan, K. S. (1969) *Indian J. Pure and Appl. Phys.*, **7**, 265.
Voigt, W. (1928) *Lehrbuch der Kristallphysik*, Verlag Teubner, Leipzig.
Vonsovski, S. V. (1971) *Magnetism*, Nauka, Moscow (in Russian).
Voronkova, E. M., Grechushnikov, B. N., Distler, G. I. et al. (1965), *Optical Materials for Infrared Technology*. Nauka, Moscow (in Russian).
Voropayeva, N. E., Reznikov, B. A., Sirotin, Yu. I. (1969) *Phys. Stat. Sol.*, **33**, 633.
Weyl, H. (1952) *Symmetry*, Princeton University Press, Princeton, New Jersey.
Wigner, E. (1931) *Gruppentheorie*, Braunschweig.
Wigner, E. (1971) *Symmetries and Reflections*, London.
Wooster, W. A. (1949) *A Text-book on Crystal Physics*, Cambridge Univ. Press, Cambridge.
Wooster, W. A. (1970) *Experimental Crystal Physics*, Clarendon Press, Cambridge.
Wooster, W. A. (1973) *Tensors and Group Theory for the Physical Properties of Crystals*, Clarendon Press, Oxford.
Yakovlev, I. A. (1956) *Dokl. Akad. Nauk SSSR*, **107**, 5.
Yakovlev, I. A. (1957) *JETP*, **32**, 4, 9.
Yakovlev, I. A. (1957a) *Usp. Fiz. Nauk*, **63**, 2.
Zagalskaya, Yu. G., Litvinskaya, G. P. (1973) *Geometrical Crystallography*, Publication of the MGU, Moscow (in Russian).
Zagalskaya, Yu. G., Litvinskaya, G. P. (1976) *Geometrical Microcrystallography*, Publication of the MGU, Moscow (in Russian).
Zamorzayev, A. M. (1957) *Crystallographia*, **2**, 15.
Zamorzayev, A. M. (1967) *Crystallographia*, **12**, 81a.
Zamorzayev, A. M. (1970) In: *Ideas of E. S. Fedorov in Contemporary Crystallography and Mineralogy*, Ed.: P. M. Tatarinova, Nauka, p. 42, Leningrad (in Russian).
Zarembo, L. K., Krasil'nikov, V. A. (1970) *Usp. Fiz. Nauk SSSR*, **102**, 549.
Zhdanov, G. S. (1961) *Solid State Physics*, Publ. of the MGU, Moscow (in Russian).
Zheludev, I. S. (1957) *Crystallographia*, **2**, 207.
Zheludev, I. S. (1964) *Crystallographia*, **5**, 501.
Zheludev, I. S. (1968) *Physics of Crystal Dielectrics*, Nauka, Moscow (in Russian).
Zheludev, I. S. (1969) *Electric Crystals*, Nauka, Moscow (in Russian).
Zheludev, I. S. (1971) *Crystallographia*, **16**, 273.
Zheludev, I. S. (1976) *Symmetry and Its Application*, Atomizdat, Moscow (in Russian).

SUBJECT INDEX

Abstract groups 49, 51
Acoustic activity 545
Acoustic axis 360, 365, 369, 370, 547, 549
Acoustic gyration 546
Adiabatic process 411
Ammonium dihydrophosphate (ADP) 178, 186, 224, 338, 345, 390, 433, 447, 524
Angle between optic axes 509
Anisotropy 19, 23, 29, 43, 175, 182
Antiaxis 465
Anticentre of symmetry 476
Antiequal figures 457
Antiferromagnetic 471, 472, 543
Antiidentification 466
Antiinversion 466, 476
Antioperations 457
Antiplane 465
Antisymmetric tensor 145, 153, 260
Antisymmetry 271, 298, 301, 456, 457, 464, 466
  point groups of 459, 464
Antitranslation 466, 486
Apophemal directions 52
Aragonite 177, 185, 245, 337
Artificial birefringence 510, 511, 513-515
Axial basis 167, 477
  directions 125, 272, 543, 590
  ratios 132
  symmetry classes 60, 62-66
  vector of acoustic gyration 546
  vectors 165, 171, 257, 262, 268, 456, 464, 479, 539, 598, 601
Barium titanate 210, 392, 424, 426, 427, 431, 558
Base-centred cell 77
Base vectors 102, 127, 585
  contravariant 88, 104, 134, 585
  covariant 22, 88, 104, 134, 585
Belov's notation 468
Beltrami-Mitchell equations 323, 330
Binormals 165, 223, 238, 242, 243
Biradials 165, 231, 238, 242, 243
Birefringence 187, 220-224, 225, 246, 510, 511, 545
Black-white groups 459-467
Body moment 318
Boldyrev's polar net 26, 179
Bravais indices 98, 108, 129
  lattices 77, 85, 92, 109, 451, 469, 581
    changes under phase transitions 451
  plane nets 77
  symbols (notation) 53
Brewster's effect 503
Brillouin zone 448
Bulk modulus 330

Calcite 178, 224, 246, 324, 364, 385
Cartesian coordinates 160, 161
Cassini ovals 249
Categories of crystals 42, 55-63, 64, 186, 187
Centre of symmetry 386, 424

Characteristic equations of tensor 148
surface (indicatrix) of tensor 163-169
Christoffel tensor 358, 367, 417, 546, 547
second 361
Chromatic polarization of light 245
Circularly polarized waves 529
Classes of magnetic symmetry 481
Close packing 133
Coefficients of depolarization 202
thermal expansion 175-178, 185, 321, 383, 437, 603
Colour symmetry 34, 37, 54, 55
Commutative groups 49
Composite (multiply composite) cell 21
Compressibility 331, 339
Conical refraction 240, 244, 245, 364
of elastic waves 363, 364
Conoscopic pictures 249, 508, 510
Contour lines 182
Coordinate directions 50
symmetry elements 52, 53, 57, 58, 86
system, hexagonal 45
rhombohedral 45, 52
systems 22, 581
Cotton-Mouton effect 542, 599
Crystal metrics 22
Crystal-physical coordinate system 135, 137
Crystallographic coordinate system 134-137, 581
matrices 140, 590
orientation 46, 551
projections 23
systems 42, 43
Cubic dielectric susceptibility 516, 599, 613
Curie groups 68, 159
point 427, 435, 436, 441, 448
principle 184-188, 201, 269, 272, 364, 394, 429, 430
Curl of tensor field 265, 313
vector field 264
Cyclic coordinates 281
Defects of crystal structure 17, 124, 175
Deformation of vector field 265
Derivative of vector field with respect to radius-vector 264
Deviator 146, 151, 195, 295, 312, 327
Dyad 144, 150
multiplication 256
Diagonal directions 52
symmetry elements 50, 51, 54, 55, 62, 86
Diamond symmetry plane 72
Dielectric impermeability 195, 202, 205, 218, 219, 220, 234, 409, 412, 503, 505, 512, 518, 598
permittivity 43, 185, 187, 191, 195, 198, 202, 208, 216, 229
susceptibility 189, 191, 598, 602
Dipole in anisotropic medium 204
Direction of by-pass of base vectors 169, 275
synchronism 631
Dislocations 126, 337, 338
Dispersion of frequency 526
optical activity 250, 251, 535
refraction index 249, 250
Displacement vector 308
Dissymmetric modification 40, 427
Dissymmetry 184, 187, 192, 429, 544, 545
Distortion, tensor 308, 319, 322
Divergence of tensor field 265
vector field 265
Domains 428, 431, 434
Duality relations 257, 268, 378
Dzyaloshinsky condition 448

Einstein's notation 93
summation rule 90, 93, 125, 126
Elastic anisotropy 329, 378
compliance 270, 271, 321, 328, 331, 332, 345, 352, 353, 383, 421, 422, 437, 557, 599

energy of crystal 490, 504
straining 320, 326
symmetry 328
waves 227, 358, 361, 416
piezoelectric corrections 409
Elasticity, coefficients 320, 328, 329, 359, 410, 599
Elastodynamics 316, 546
Elastooptical coefficients 504, 616, 635
Elastoresistive coefficients 635
Elastostatics 316, 323, 396
Electric conductivity 42, 187, 210, 324, 491, 496, 598, 602
Electric enthalpy 406
field strength 188, 216
resistance 598
Electrocaloric effect 385
Electrogyrational effect 540, 543, 599, 613
Electromechanical coupling coefficients 403, 418, 423, 635
effects 395
Electrooptical effects 188, 503, 505, 506, 538, 539, 601, 607, 635
Electrostriction 489, 599, 611
Electrothermal effects 395
Elliptic polarization 528, 548
Ellipticity 528, 548
Enantiomorphism 65, 68, 71, 124, 298, 536, 537, 562, 563, 581
of quartz crystals 86
Enthalpy 406
Equations of compatibility of strains 351
elastic equilibrium 351
indicatrix 220, 221
Equivalent symmetric directions 43
E. S. Fedorov's net 27, 28
notation 84, 85
Euclidean groups 457, 466
Eulerian angles 142, 143
Euler's theorem 41
Expanded orthogonal group 457, 476
Expansion of tensor into irreducible components 326

Face parameter 97, 98
(plane) symbol 21, 92, 95
Faraday's effect 540, 542, 593, 602
Fedorov's groups 84, 467
Ferroelectrics 190, 210, 382, 413, 441
phase transitions 441, 455
Figures of mixed polarity 459
Forces conjugate to fluxes 494
Free energy 406
Fresnel's ellipsoid 163, 227-231, 236, 241-243
equation 236
Friedel's law 68
Fumi's method of direct verification 275, 276, 303

Gauss-Ostrogradsky theorem 265, 315
Generation of second harmonic 518
Generators of symmetry groups 50, 267, 278, 287, 305
Gibbs' free energy 381, 407
Glide elements 337
reflection plane 71, 79
systems 337
Gnomonic projection 24, 27, 28
Gnomostereographic projection 25-27, 127, 129
Green's tensor 324
Grey groups 459
Groth's notation 56-59, 65, 108
Group representation 287, 305
of rotations 71
velocity of elastic waves 361
Groups of tensor's external symmetry 159, 269, 279, 288

Hall's coefficients, tensor 408
effect 498, 598, 599

Heat exchange conditions, coefficient 214
Helical structures 475
Helmholtz's free energy 407
Hemihedry 56, 119, 563
Hermann's theorem 281, 284, 327, 365, 387, 394, 396, 537, 559
Hooke's law, generalized 319, 321, 323, 332, 351, 352, 478, 489, 545, 577, 578
  with small corrections 579
  temperature terms 351
Hydrostatic pressure 405

Incompatibility of tensor field 265, 290
Indexing 92
Identification 38, 48
Intersection of groups 45, 50, 185-188
International notation 51-54, 84-86
Interplanar distances 130
Inversion 36, 139, 283
  of basis 169
  operations 36
  rotations 466, 479
  symmetry axis 39, 40
Irreducible representation 448
Isomorphous groups 51, 123
Isothermal process 412
Isotropy axis of second-rank tensor 164

Jahn's notation (symbols) 259, 260, 598

Kerr effect 507, 510, 514, 599, 635
Kinetic coefficients 494, 501
Kirchhoff-Volterra-Cesar formula 313
Kronecker's symbol 88, 107, 126, 134, 139, 303, 307, 326

Lagrangian multipliers 156, 158, 233-235, 368, 551, 553
Lamés coefficients 330
Landau condition 448
Laue symmetry classes 68, 186, 268, 346, 350, 485, 501-503
Law of the constancy of angles in crystals 19, 23
  doubling 439
  Haüy 96, 97
  of rationality of parameters 96
Legendre's polynomial 301
Levi-Civita pseudotensor 262
  symbols 103, 129, 139, 261, 305, 307, 326
Lifshits condition 448, 450, 453
Limit classes of symmetry 182
  groups 68-71, 159, 185, 192, 288, 556
  point groups 68, 460
Lloyd's experiment 244
Longitudinal normal 359, 368, 371

Magnetic charge 463, 481
  field intensity 216
  ordering 475
  resistance 502
  symmetry groups 460, 476, 480
Magnetically ordered crystals 545
Magnetocaloric effect 485
Magnetoelectric effect 485
Magnetostriction 596

Malus' law 246
Mandel'shtam-Brillouin scattering 505, 550
Matrices of orthogonal transformation 137, 140
Matrix, square 102
  trace 139
Maxwell's equation 216, 218, 229, 527
Metric tensor 90, 104-107, 132, 133
Miller indices 22, 93-96, 104, 106-114, 125, 127, 198, 333, 338
    determination of normal tensor components 198
    transformation 110
Mirror-rotation axis 40
Modulus, bulk 330
Moment stresses 318, 319
Multiplication of symmetry elements 78
    tensors 256
Mutually reciprocal matrices 102

Nernst-Ettingshausen effect 498, 599, 611
Neumann's principle 185, 186, 192-194, 270
Neutral groups 459
Nonor 295, 297, 299, 300, 326, 345
  part of tensor 326

Ogdohedry 56, 119, 565
Ohm's law in crystals 210
Onsager reciprocal relations 493
Operation of reflection in a plane 36
Operations of antiidentification 458, 459, 465
Optic axis 163, 165, 222, 231, 238, 370, 508-510, 521, 548
    comparison with acoustics 370
Optic sign of crystals 225
Optical indicatrix 163, 220-226, 503-506, 510, 512
    equation 232, 233, 241
    disturbed 511
  representation of tensor 164
  surfaces 241, 243
Orthogonal transformation 137, 138, 168, 269, 460, 476
Orthonormalized basis 134, 137, 149
Ovaloid of refraction indices 240
    wave velocities 240

Paraelectrics 438, 441
Paramagnetics 470
Parameter of dissymmetry 430, 434
Paramorphism 565
Period of identity 19, 133
Phase transitions 87, 423, 424, 442, 445
    of the displacement type 424
        first kind 423
        "order-disorder" type 425
        second kind 427
    without change of translation symmetry 427
Phase velocity 217, 228
    of elastic wave 358, 360, 368, 370-372, 376, 377
Photoelasticity 616
Physical symmetry groups 457
Piezocaloric effect 487, 599
Piezoelectric effect 272, 384, 386-391, 394, 403, 404, 405, 409, 411, 416, 421, 422, 437, 444, 506, 551-555, 598, 599
Piezogyration 543
Piezomagnetic effect 485, 599

Piezooptical effect 188, 272, 289, 503, 509, 515
Piezoresistive effect 451, 493, 599, 635
Plane net 20, 23, 75, 89
  cell 20, 21
Plane waves 216, 232
  of vibrations 218
  point charge in anisotropic medium 204
  group symbol 51
  groups 47, 52, 56
    of antisymmetry 68
    crystallographic 47, 52, 461
    of magnetic symmetry 460
  symbol 21
  symmetry 83
Poisson's ratio 330, 334, 335, 346-348, 423
Polar figures 458
  groups 475
Primitive cell 20
Principal minor 422
Principle of duality 229, 240, 378
    symmetry of kinetic coefficients 486
Pseudodeviator 577
Pseudodonor 297, 298-301, 547
Pseudoseptor 297, 300-302
Pseudoscalar 17, 257, 259, 314, 315, 547
Pseudotensor 253, 257, 315, 547
  of gyration 526, 534, 538, 598, 603
Pseudovector 257
Pyroelectric effect 191, 192, 208, 210, 381-384, 395, 402, 412, 413, 421, 422, 438, 598, 601
Pyromagnetic effect 485, 598

Quadratic dielectric permittivity 489, 598, 599
  susceptibility 516, 522, 605, 607
Quartz 36, 87, 181, 183, 364, 376, 426, 445, 456, 472, 532, 537, 549, 550, 561
Quasilongitudinal waves 359
Quasitransversal waves 359

Radius of discreteness 17, 18
    homogeneity 17, 18
Ray surface 236, 239, 242
  vector 227
  velocity 228, 231, 240
    of elastic wave 361, 371, 372, 377
Reciprocal lattice 88, 90, 130
    cell 81-92
Reflection-rotation axis 40
Regular system of points 88
Resolution of base vectors 102, 106
Reverse symmetry operations 48
Righi-Leduc effect 438, 598, 599
Rochelle salt 86, 87, 177, 185, 390, 426, 433
Rock salt 17, 72, 364, 472
Rotation of polarization plane 68, 171, 274, 531, 537, 538, 598
    of elastic waves 549
Row (of material particles) 20
  parameter 19
  symbol 22, 92
r-rank tensor 267, 270, 295

Saint-Venant's equations 313, 323
  principle 339
Sapphire 180, 181, 364
Scalar 326, 346
  product of tensors 263

Schoenflies notation 54, 65,69, 84
Screw directions 536, 543, 595
  symmetry axis 73, 366, 367
Second-rank tensor, covariant components 106, 107, 143
    isotropic planes 164, 301
    mixed components 106
    normal components 155, 234
    representation surface 161-164, 165, 188, 271, 298, 325
      sections 174, 175, 181, 272
    tangential components 157, 234
Septor 295, 297, 299, 300, 547, 552
Shear 334
  modulus 330, 335, 337, 343, 632
  stresses 338
Shubnikov groups 466, 469, 473
  notation 54, 74
Space group symbol 85
  groups 84
  lattice 21-23, 33, 74
Spatial dispersion 525, 526
Specific resistance, tensor 210
Spherical coordinates 161
Spontaneous polarization 190, 207, 382, 444, 455, 591
  strain 444, 598
Square matrices 102
Stenon's law 19
Stereographic projection 24, 65, 71 127, 177, 272, 300, 465
Stiffness 320, 328, 340, 342, 406, 490
Strain heat 383
Strain, tensor 309, 311, 312, 628,
  of vector field 264
Stress tensor 314, 628
Supergroups 50
Sylvester's theorem 420
Symmetric modification 421, 427
  tensor 145, 257, 557, 558
  transformation (infinite) 71, 84
Symmetry classes 47, 55, 56, 60-66
  elements 27, 36, 60, 73
  operation, product 36, 37, 41, 42
  operations 29, 36
    reverse 48
  plane 30, 31, 38, 53, 72, 79, 424, 459, 559, 561
  reflection axis 31, 38, 53, 54
  of representation surfaces 185
    X-ray photographs 186

Thermal diffusivity 213
  stresses 351
  tensor, alternated 256, 257
  biaxial 164
  contracted 256, 262
  deviator part 326
  differentiation 248, 249, 259
  eigenvalue 147, 152, 154, 157
  eigenvectors 147, 152, 157
  electric type 481
  even type 268, 290, 293, 481
  field 191, 265, 312
  gyrotropic 193, 194, 306, 323, 400
  invariant components 91
  isomers 256
  isotropic 160, 301
  of magnetic type 484
    magnetoelectric type 480, 484
  matter 191, 193, 270, 284, 295, 556, 560, 577, 578
  odd type 268
  reciprocal 145
  of small rotations 309
    small strains 308, 628
  spherical 145, 160
    part 146, 151
  sum 255
  two-dimensional 164
  uniaxial 164

Tensor function 255
Tensoresistive effect 491
Tensors, addition 255
averaging over the group 287
biscalar product 263
contracted notation 627
Tensors, external symmetry 159, 266
internal symmetry 258, 326, 386, 489
irreducible 295, 297
invariant 159, 600
components 90, 91
mutually reciprocal 145
non-coordinate notation 263
product 256
Tension coefficients 176, 179, 186, 271, 347, 349
Tetartohedry 57, 119, 565
Theorem on the multiplication of symmetry operations 597
uniqueness 330
Theory of group representation 287, 446, 547
Thermal (heat) capacity 395, 409
thermal conductivity, tensor 187, 195, 212, 325, 598, 602
stresses 214
Thermoelasticity 322, 354, 410, 610
Thermodynamic coordinates 380
forces 380, 397, 406, 494
matrices 382, 397, 406, 485
potentials 407
Thermoelectric coefficients 598
Thermogalvanomagnetic coefficients 500
Third-rank tensor 254
Time inversion 456, 463, 471, 476, 477
reversal 456
Tourmaline 178, 186, 272, 347, 392, 465, 556
Transformation of indices 101, 105, 111, 129, 276
Translation 20, 71-75, 80, 184
group 21, 74
Transpose of a matrix 138
Transversally isotropic bodies 328
tensors 160
Twist 341-343, 346-348
coefficients 176, 180, 185, 271, 343, 345, 347-349
modulus 176

Uniaxial tension 331, 345
Uniform compression 331
modulus 331
expansion 331, 335, 347, 348
Unit cell 20, 33, 77
volume 88, 101
Unique (singular) directions 42, 54, 590
element of a group 51
face 96
matrices 102
operation 36, 48
scalar 346
tensor 145, 301, 302
volume 174

Vector field 264, 312
function, general 576
of polarization 359
potentials 567
of pyroelectric coefficients 209, 598
small rotations 309, 598
Vectorial basis of lattice 21, 88, 101, 477, 478
Velocities of elastic waves 633

Verdet constant 542
Volume expansion (compression) 339

Wave normal 232, 358, 530, 547, 548
  surface 228, 236, 241, 377
    of elastic waves 377
  vector 217, 358, 359
White groups 459
Wulff-Bragg formula 92
Wulff net 26, 129

X-ray photograph symmetry 186

Young's modulus 175, 179, 186, 330, 332, 340, 343, 421, 423
  representation surface 185, 343

TO THE READER

Mir Publishers welcome your comments on the content, translation and design of this book.

We would also be pleased to receive any proposals you care to make about our publications.

Our address:
Mir Publishers
2 Pervy Rizhsky Pereulok
I-110, GSP, Moscow, 129820
USSR

Printed in the Union of Soviet Socialist Republics

A Modern Handbook of Physics. For Engineering Students

B. YAVORSKY, D.Sc. and A. DETLAF, Cand.Sc.

This is a modern handbook of physics in the sense that it covers both the principles of classical physics and the fundamentals of those branches of modern science called atomic and nuclear physics, quantum mechanics, solid-state physics, particle physics, special relativity, quantum optics, etc. In scope and depth it includes all the definitions, formulas and data usually found in up-to-date physics courses of engineering institutes and of the engineering departments of universities and colleges. Physical laws are concisely formulated, necessary explanations are given and, in some cases, derivations as well. All the physical units and symbols comply with the requirements of the SI.

This comprehensive handbook was designed primarily for engineering students, as well as college and university students, studying, but not majoring in physics. It can, however, be used to advantage by engineers and graduate students not specializing in some branch of physics, and by lecturers and instructors of intermediate schools and colleges.